The temperature dependence of chemical shifts: mechanisms and contributions

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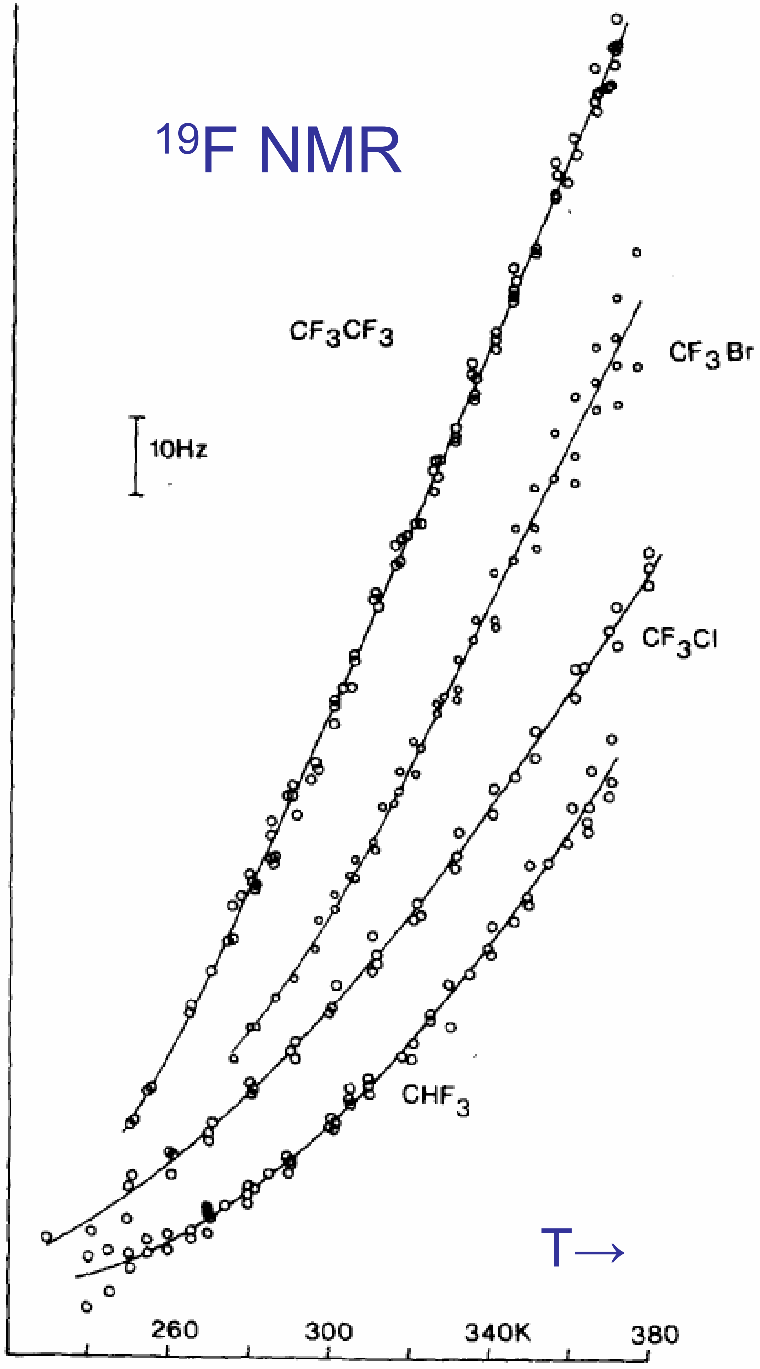
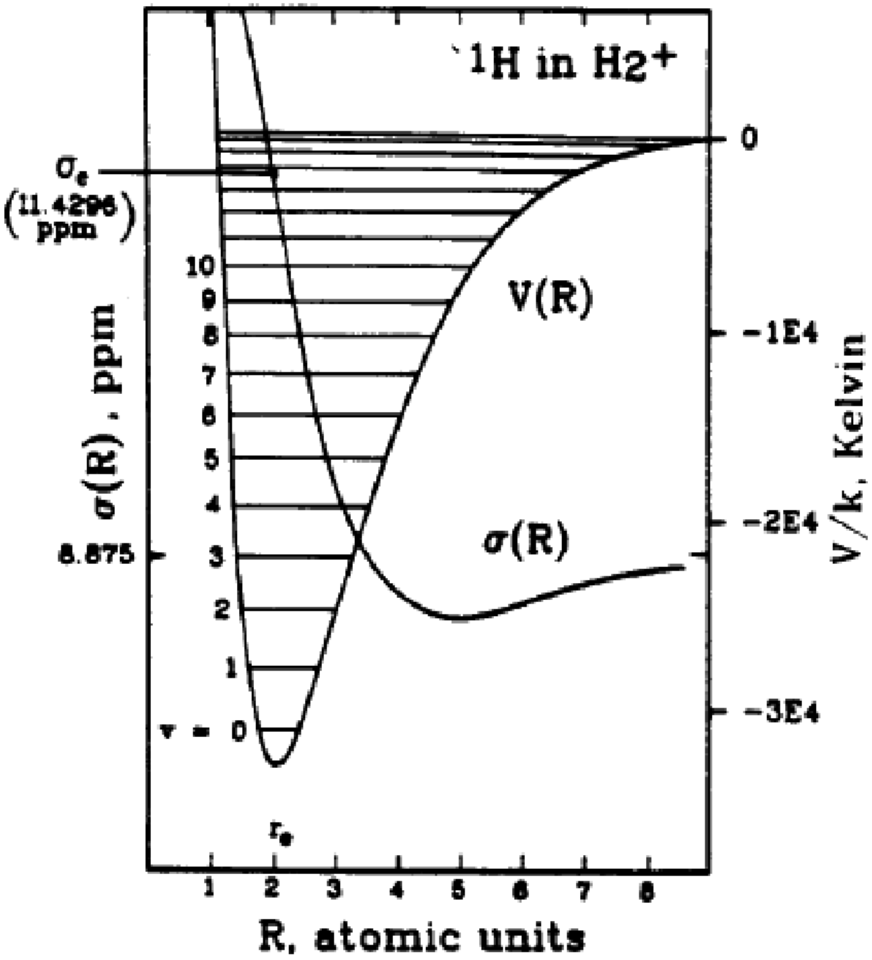


outline

- the intramolecular shielding surface
- temperature dependence of the average chemical shift in an “isolated” diatomic molecule
- in an “isolated” polyatomic molecule
- temperature dependence of intermolecular chemical shifts in a constant volume homogeneous system
- temperature dependence of intermolecular chemical shifts in a constant pressure homogeneous system; the major contribution from expansion of the solvent
- temperature dependence in heterogeneous systems: one Xe in a cage; n Xe in a cage
- Xe in a channel; the major contribution from temperature dependence of the adsorption isotherm

I. the intramolecular shielding surface



for H_2^+ molecule the shielding function is known all the way from the value 8.875 ppm at infinite separation through the 11.4296 ppm at the equilibrium geometry, and 35.5009 ppm for the united one-electron atom, He^+.

R. A. Hegstrom, Phys. Rev. A 19, 17-30 (1979)

Dynamic averages

To get the average value of a molecular electronic property:

$$\langle P \rangle_v = \int_{-\infty}^{+\infty} \left| \Psi_v(x) \right|^2 P(x)\,dx$$

We can also find the rotational average.

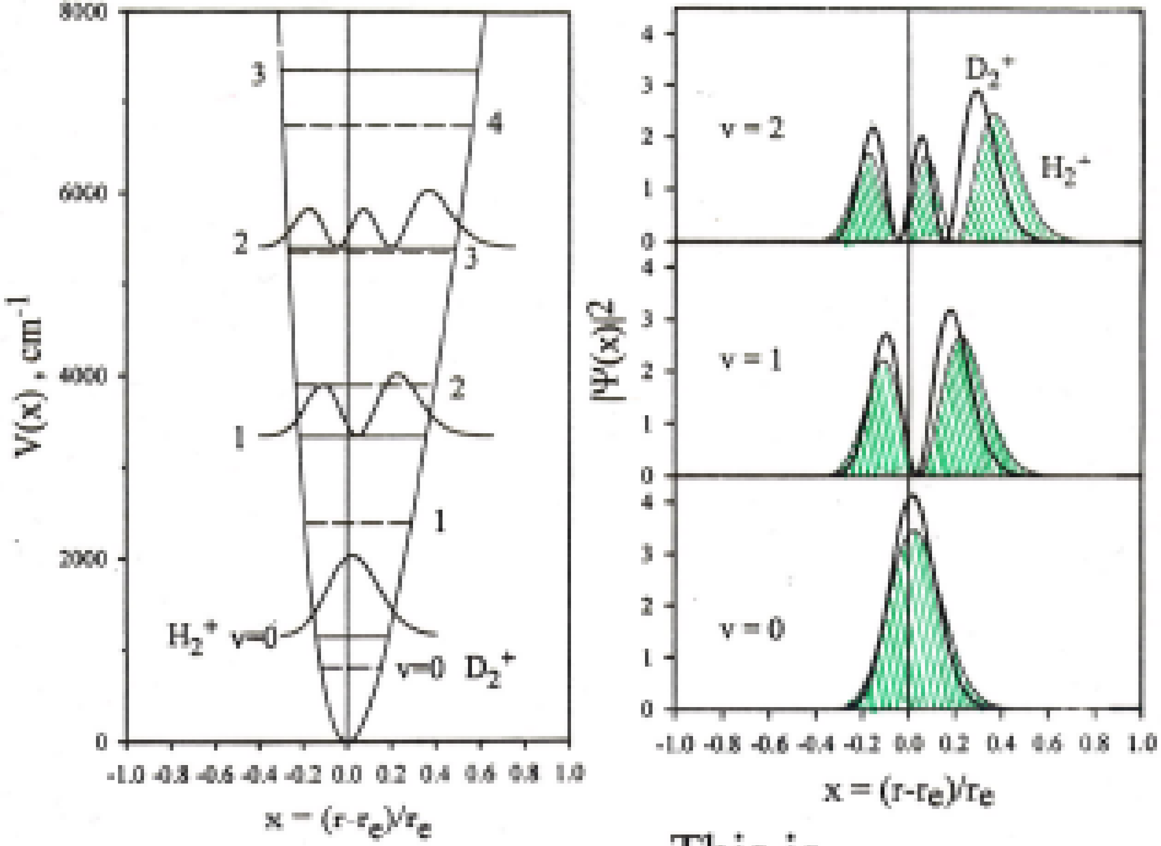
The thermal average is

$$\langle P \rangle^T = \frac{\sum_{v,J,K} (2J+1) g_{Ns} \langle P \rangle_{vJK} \exp(-E_{vJK}/kT)}{\sum_{v,J,K} (2J+1) g_{Ns} \exp(-E_{vJK}/kT)}$$

We can see that the low frequency vibrations are important, but also those vibrational modes that have large $\langle P \rangle_{vJ}$

H_2^+ vibrational wavefunctions

The probability of finding a molecule at a given nuclear configuration is given by $|\Psi_{vib}|^2$.



This is mass-dependent.

vibrational averaging occurs around the equilibrium bond distance

- For a given v,J state, the averaging weights the **extended bond** values of shielding more than the compressed bond values of shielding because of

    (a) anharmonicity of the vibration

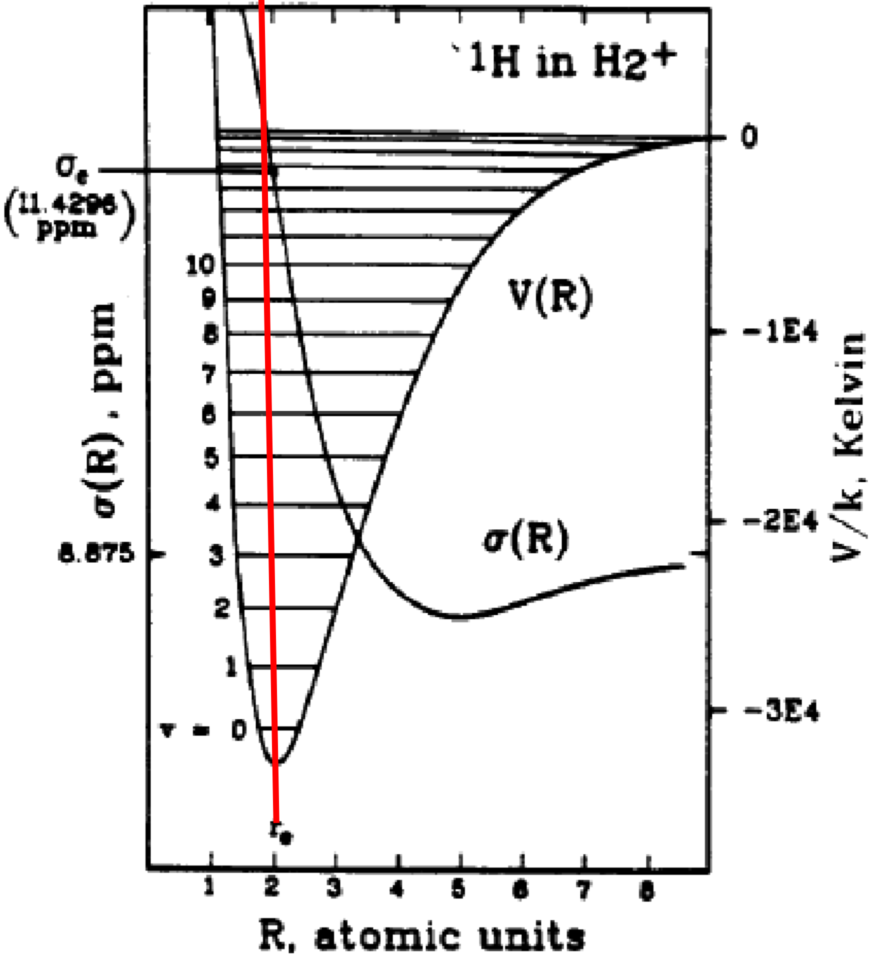
    (b) centrifugal stretching

  That is, the average bond length is longer than the equilibrium bond length, becoming more pronounced at higher v levels.
- Going to **higher temperatures** weights the higher vibrational levels more, thus **shifting further away from the shielding value at the equilibrium bond length**.

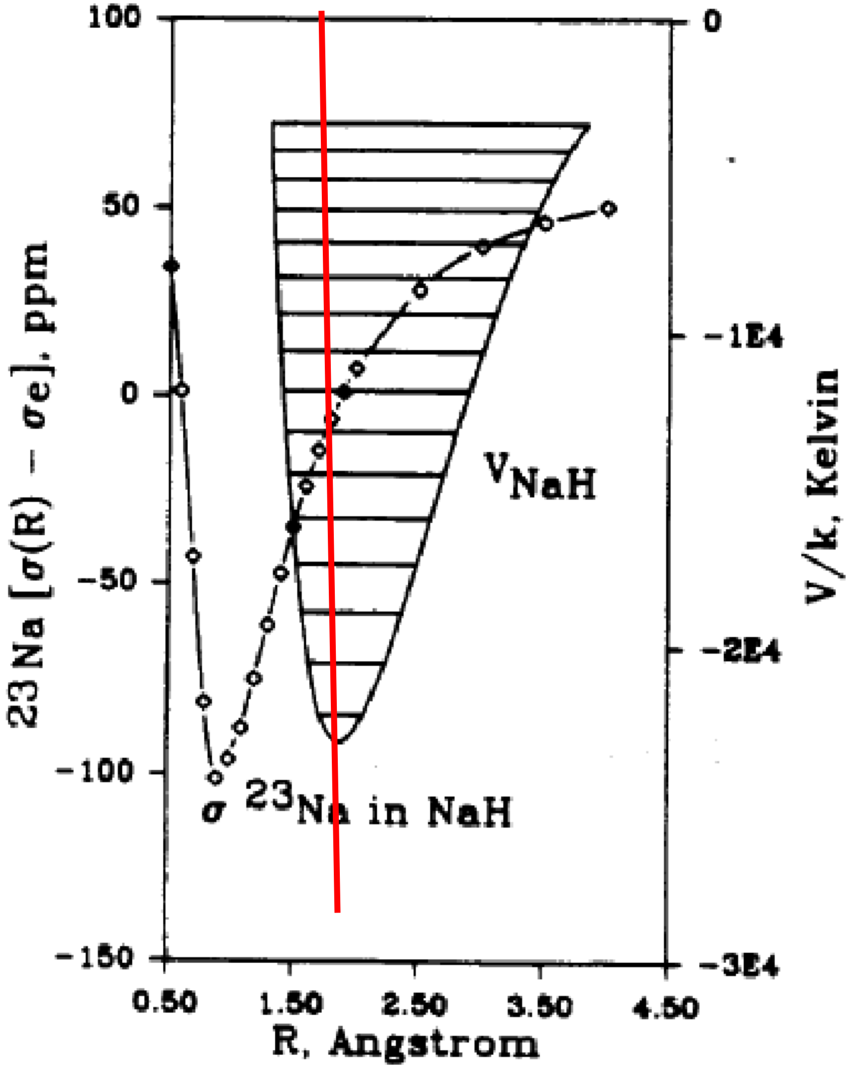
the temperature coefficient of the chemical shift

- sign will depend on the sign of the derivative of the shielding function at the equilibrium geometry
- magnitude will depend on the magnitude of the derivative of the shielding function at the equilibrium geometry and the anharmonicity of the vibration

in the vicinity of the equilibrium geometry

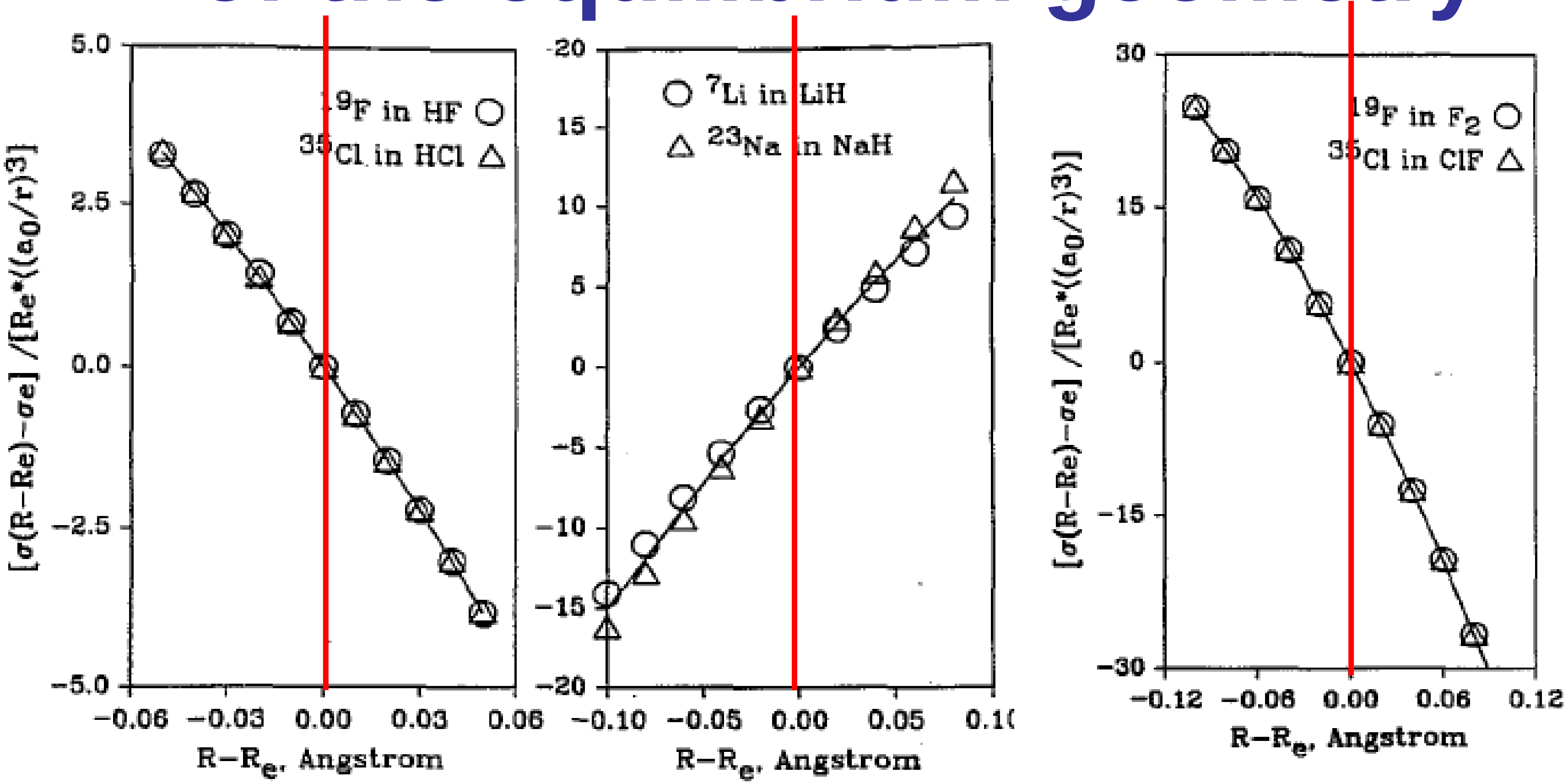


proton becomes less shielded with increasing bond length



^{23}Na becomes more shielded with increasing bond length

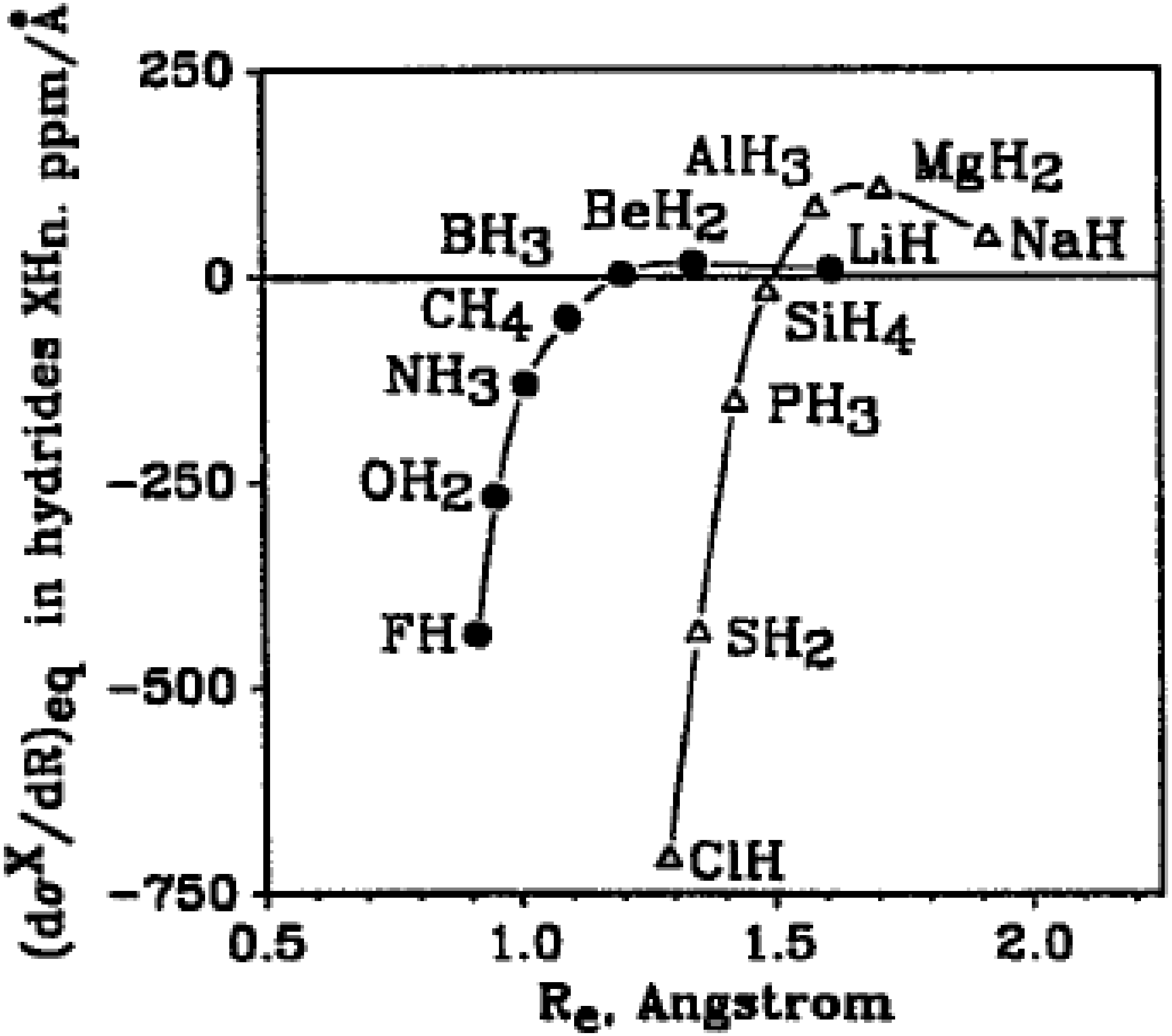
shielding changes in the vicinity of the equilibrium geometry



HF, HCl, LiH, NaH, F_2, ClF

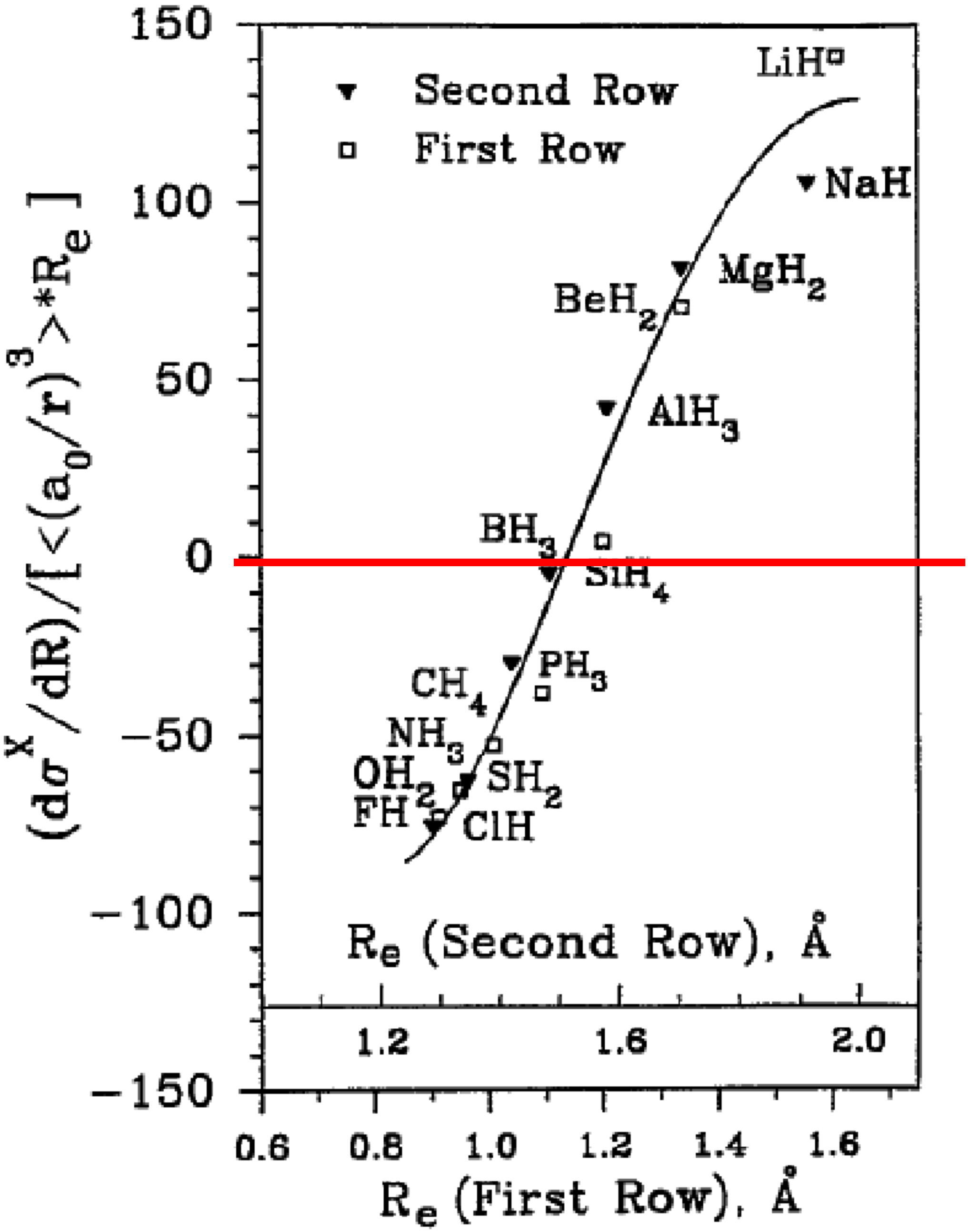
scaling permits direct comparison of F with Cl, Li with Na,

compare shielding derivatives across the Periodic Table

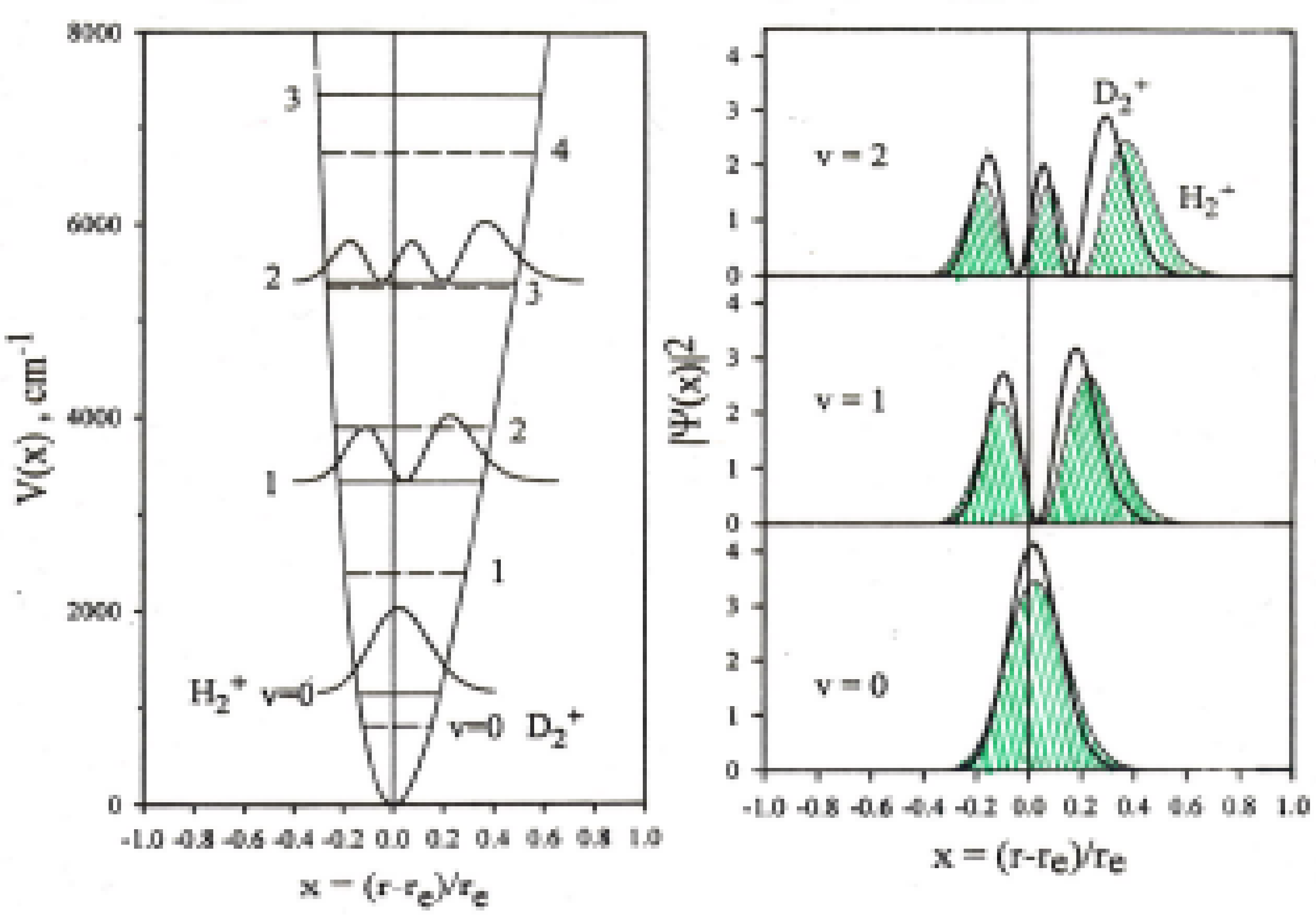


scaling places first and second row on same graph

greater shielding with bond stretch leads to **decreasing chemical shift with increasing T**

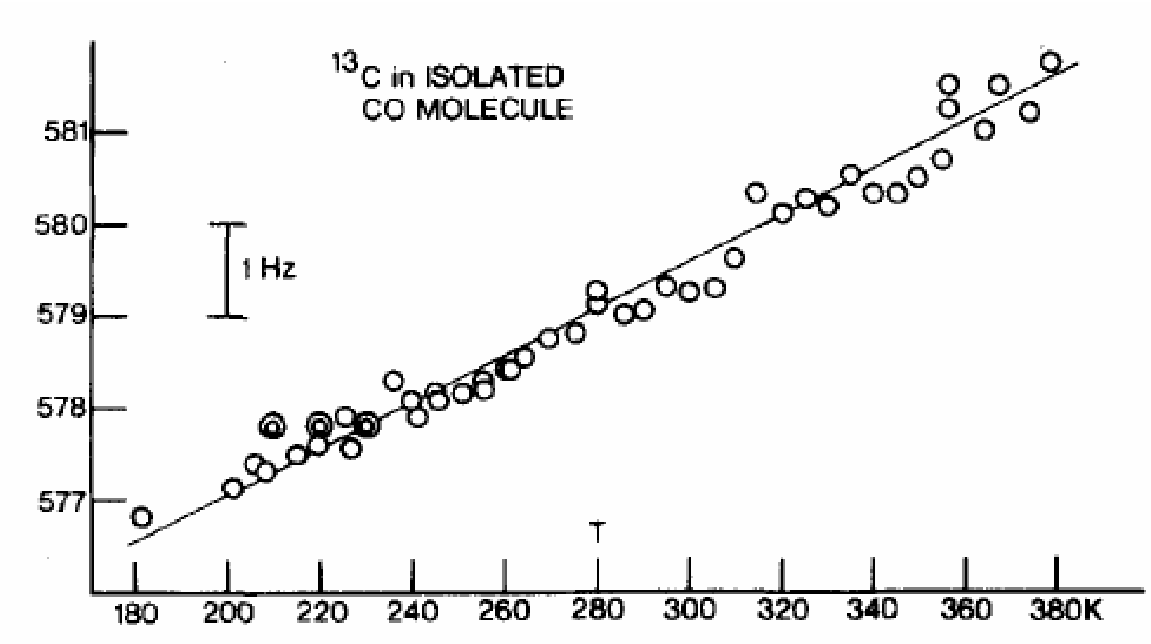


less shielding with bond stretch leads to **increasing chemical shift with increasing T** sign of chemical shift with lighter atom substitution is same as with increasing temperature, **both correspond to greater average bond lengths**



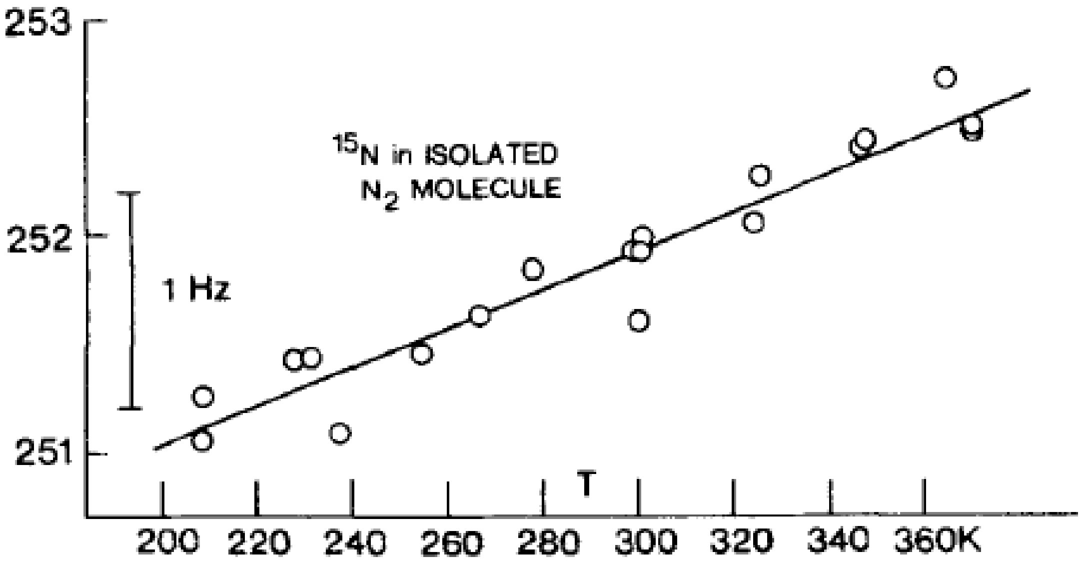
II. T dependence of chemical shift in an isolated diatomic molecule

^{13}C in isolated CO molecule



increasing chemical shift with increasing T

^{15}N in isolated N_2 molecule



increasing chemical shift with increasing T

diatomic molecule rovibl averaging

$\xi = (R - R_e)/R_e$ is[32]

$$\sigma(\xi) = \sigma_e + (d\sigma/d\xi)_e\, \xi + \tfrac{1}{2}\,(d^2\sigma/d\xi^2)_e\, \xi^2 + \cdots$$

$$\xi_{v,J} = -3a_1(B_e/\omega_e)\,(v + \tfrac{1}{2}) + 4(J^2 + J)\,(B_e/\omega_e)^2$$

$$\xi^2_{v,J} = 2(B_e/\omega_e)\,(v + \tfrac{1}{2}) \quad , \quad a_1 = -[1 + (\alpha\omega_e/6B_e^2)]$$

$$\langle v + \tfrac{1}{2}\rangle = \tfrac{1}{2}\coth(hc\omega_e/2kT)$$

$$\langle J^2 + J\rangle = kT/hcB_e \quad ,$$

$$\langle\sigma\rangle^T - \langle\sigma\rangle^{300} = (B_e/2\omega_e)\,[(d^2\sigma/d\xi^2)_e - 3a_1(d\sigma/d\xi)_e]$$

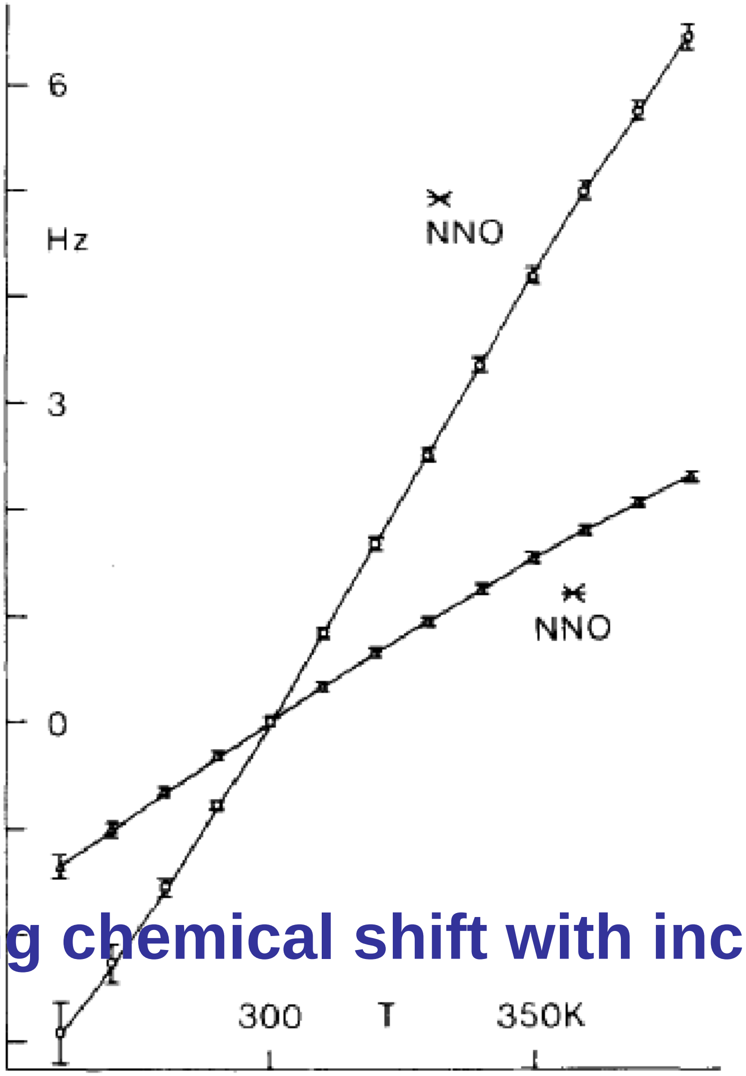
$$\times [\coth(hc\omega_e/2kT) - \coth(hc\omega_e/2k300)]$$

$$+ (4k/hc)\,(B_e/\omega_e^2)\,(d\sigma/d\xi)_e(T - 300) \ .$$

III. an isolated polyatomic molecule

- experimental observations in samples of various known densities, followed by extrapolation to zero density finds a temperature dependence that is intrinsic to an isolated molecule

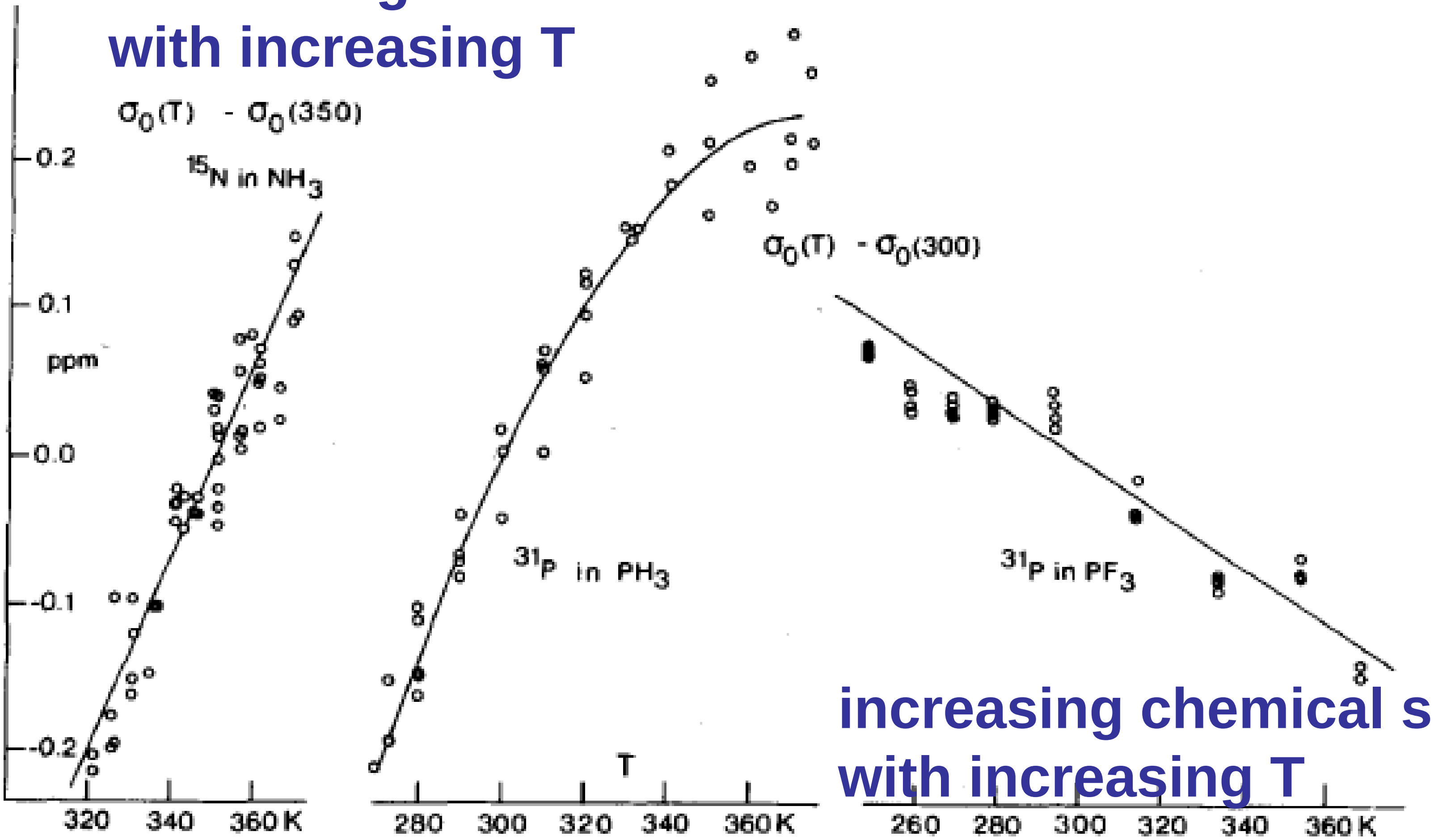
^{15}N in isolated NNO molecule



increasing chemical shift with increasing T

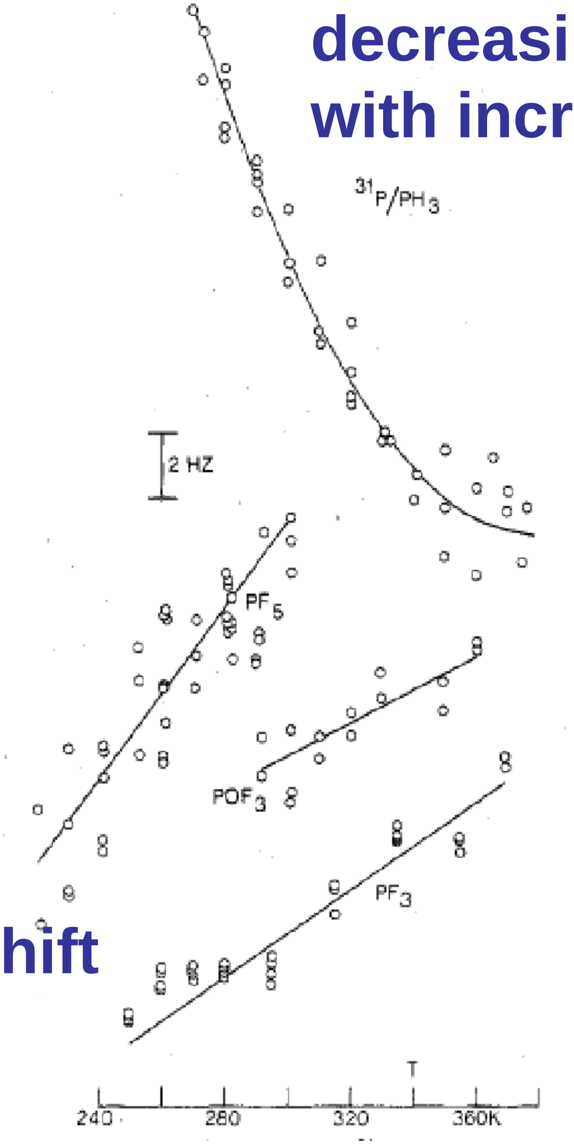
^{15}N in NH_3, ^{31}P in PH_3 and PF_3 isolated molecules

decreasing chemical shift with increasing T



increasing chemical shift with increasing T

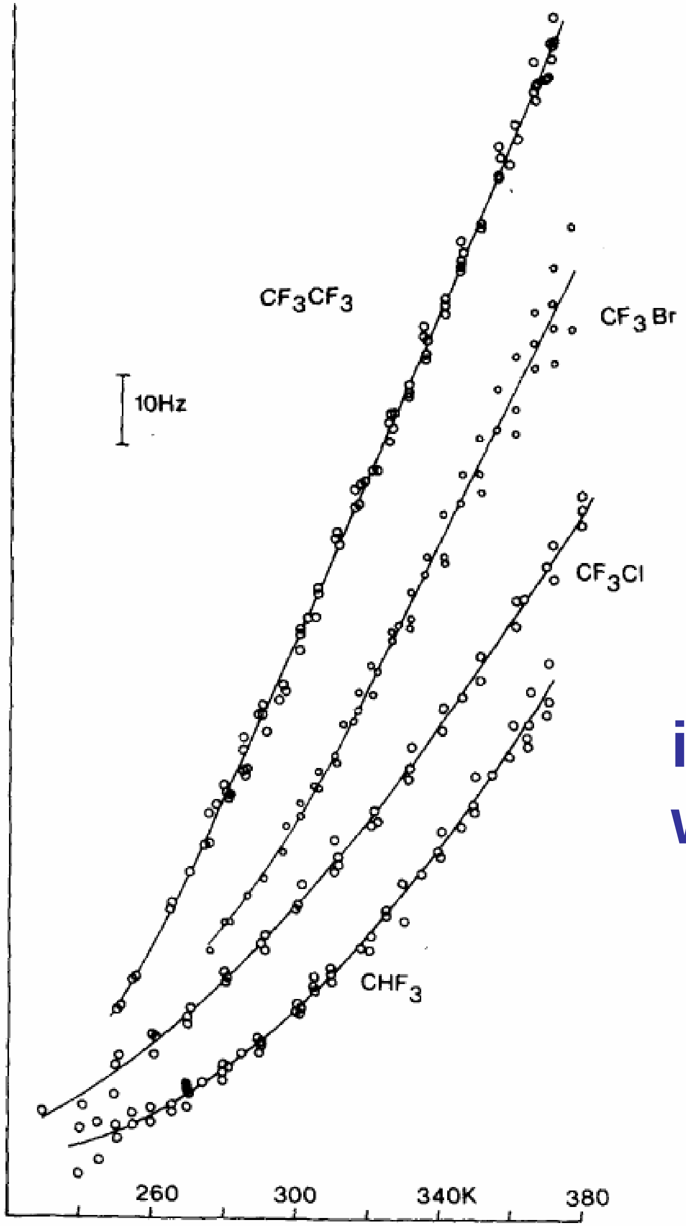
^{31}P in isolated molecules



decreasing chemical shift with increasing T

increasing chemical shift with increasing T

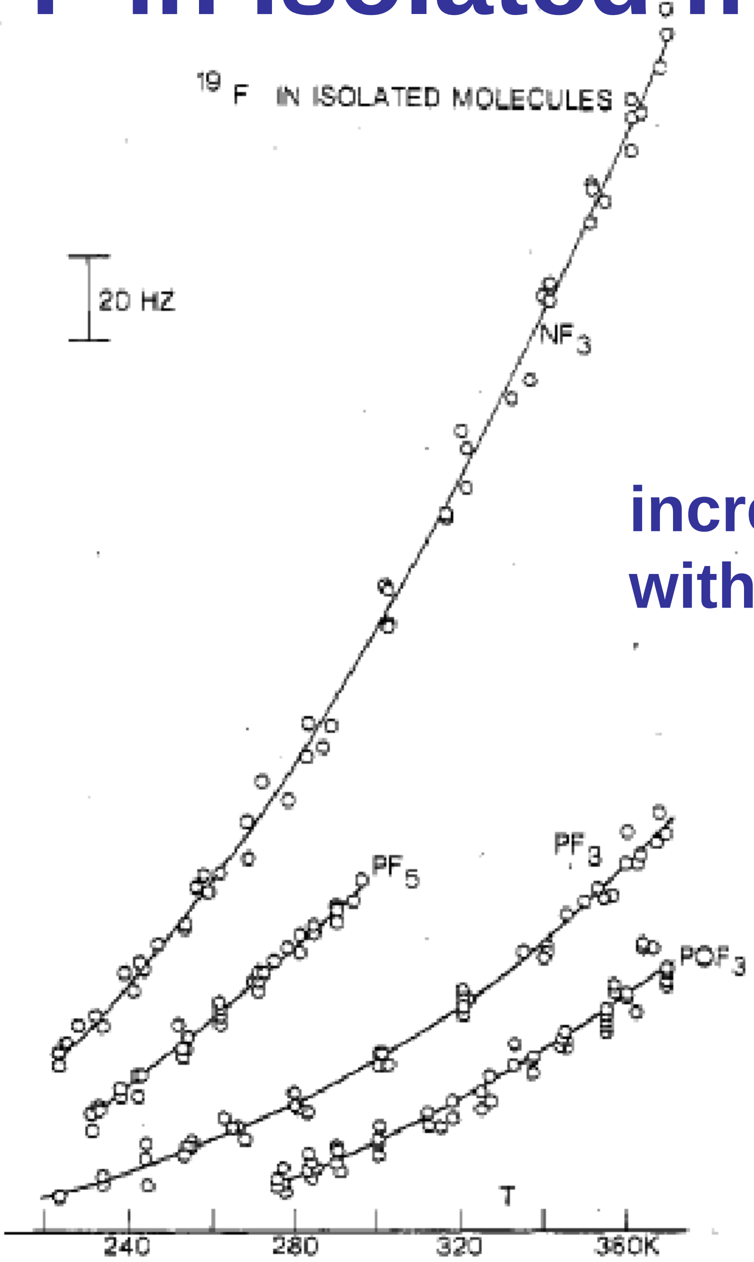
Temperature dependence of ^{19}F



fluoroalkanes

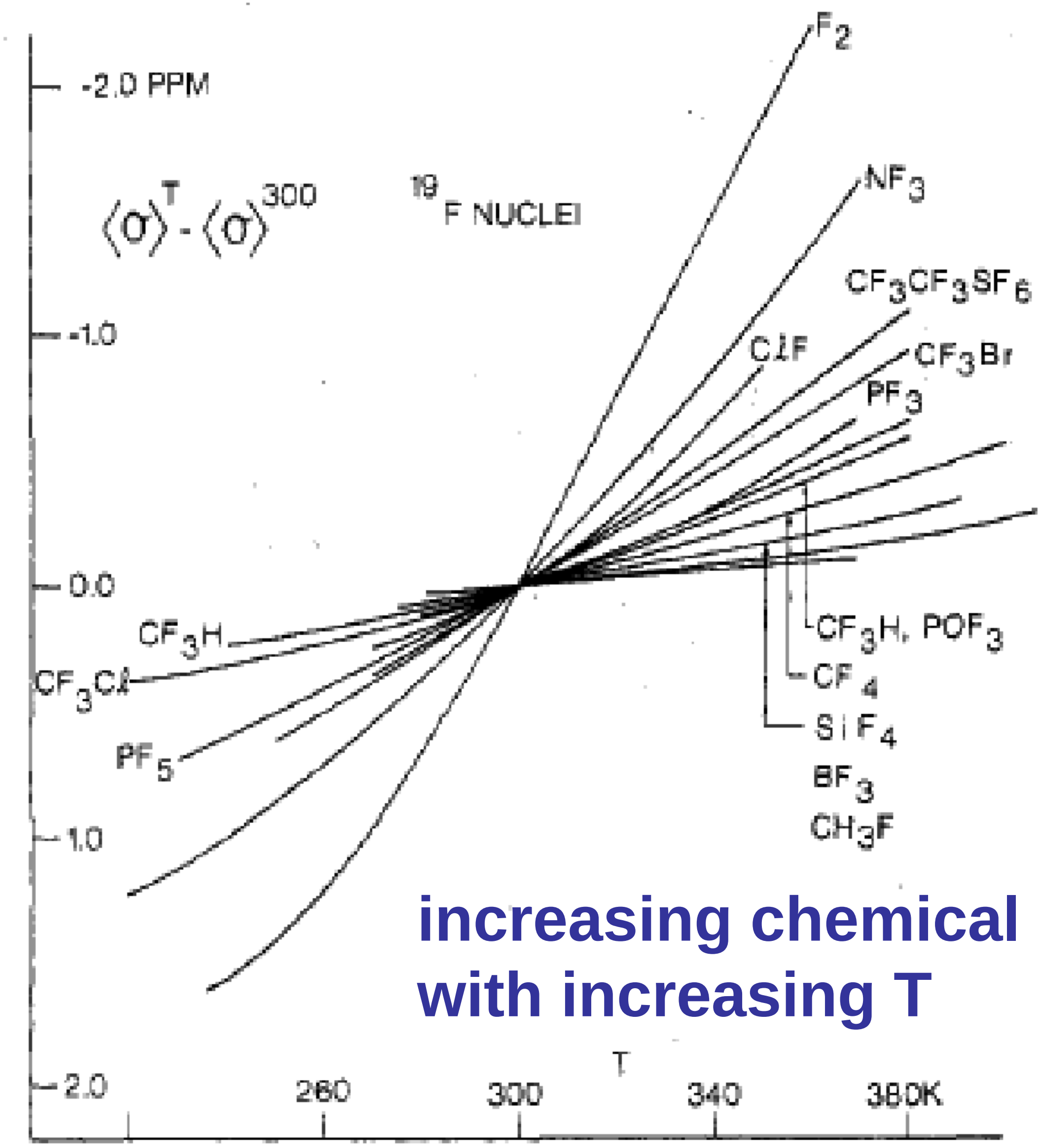
increasing chemical shift with increasing T

^{19}F in isolated molecules



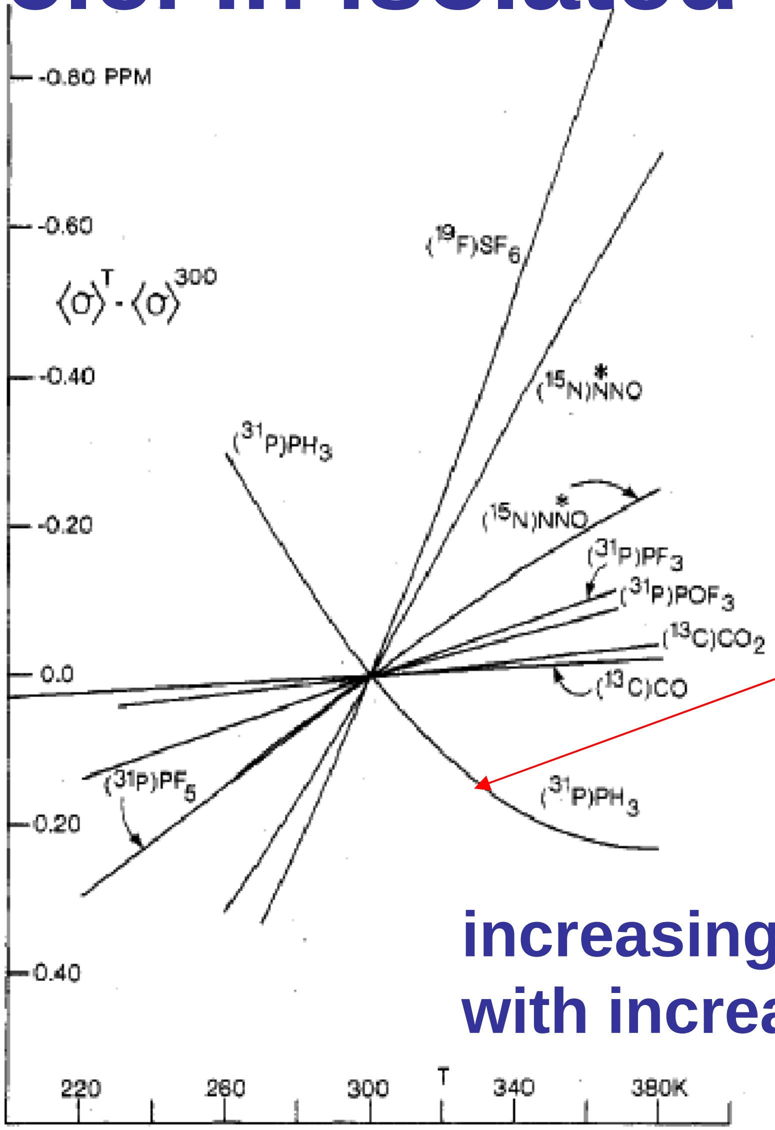
increasing chemical shift with increasing T

Temperature dependence of ^{19}F



increasing chemical shift with increasing T

various nuclei in isolated molecules



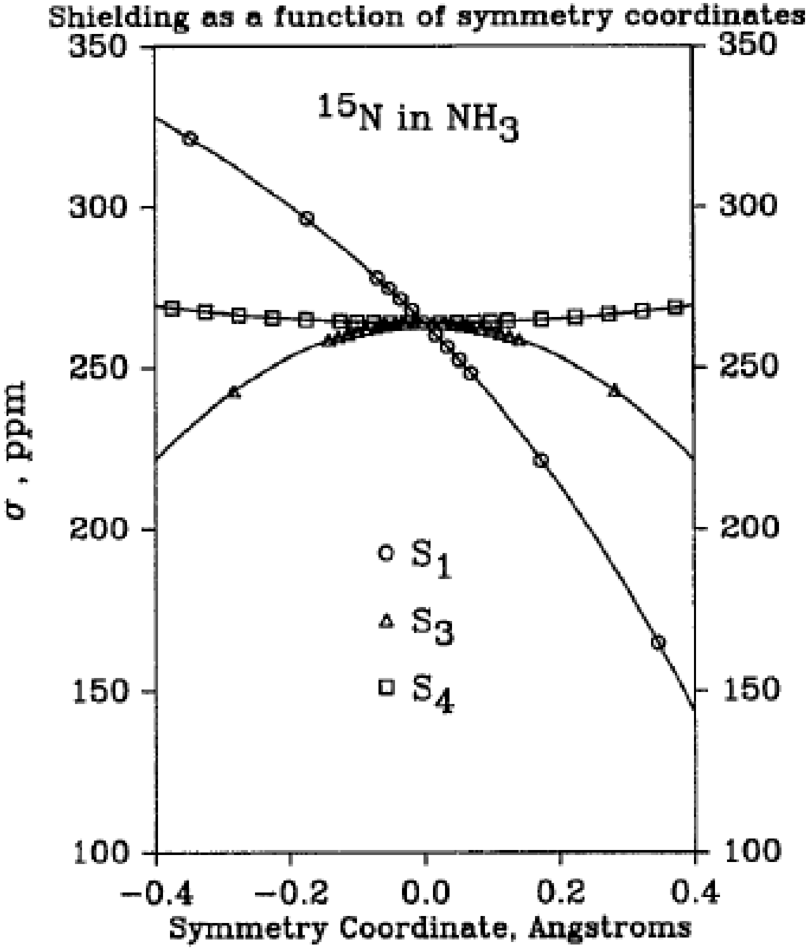
but not for ^{31}P in PH_3

increasing chemical shift with increasing T

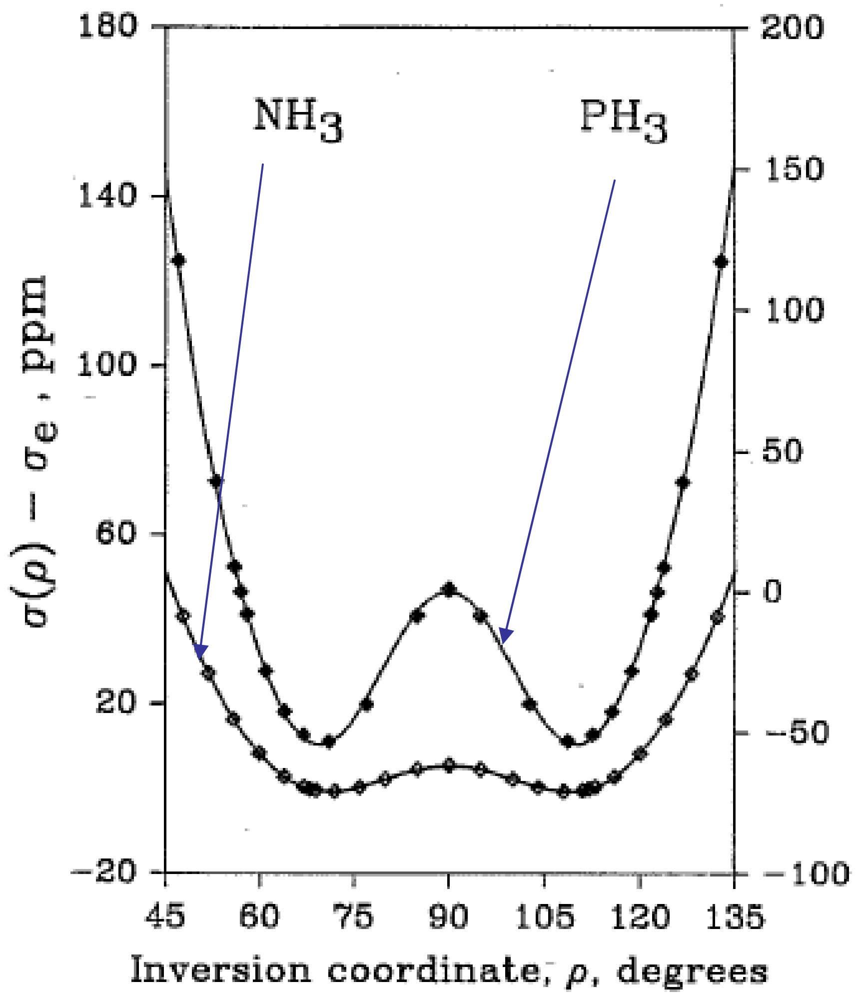
quantum mechanical calculations of shielding surfaces in polyatomic molecules

- NH_3, PH_3
- CH_4, OH_2

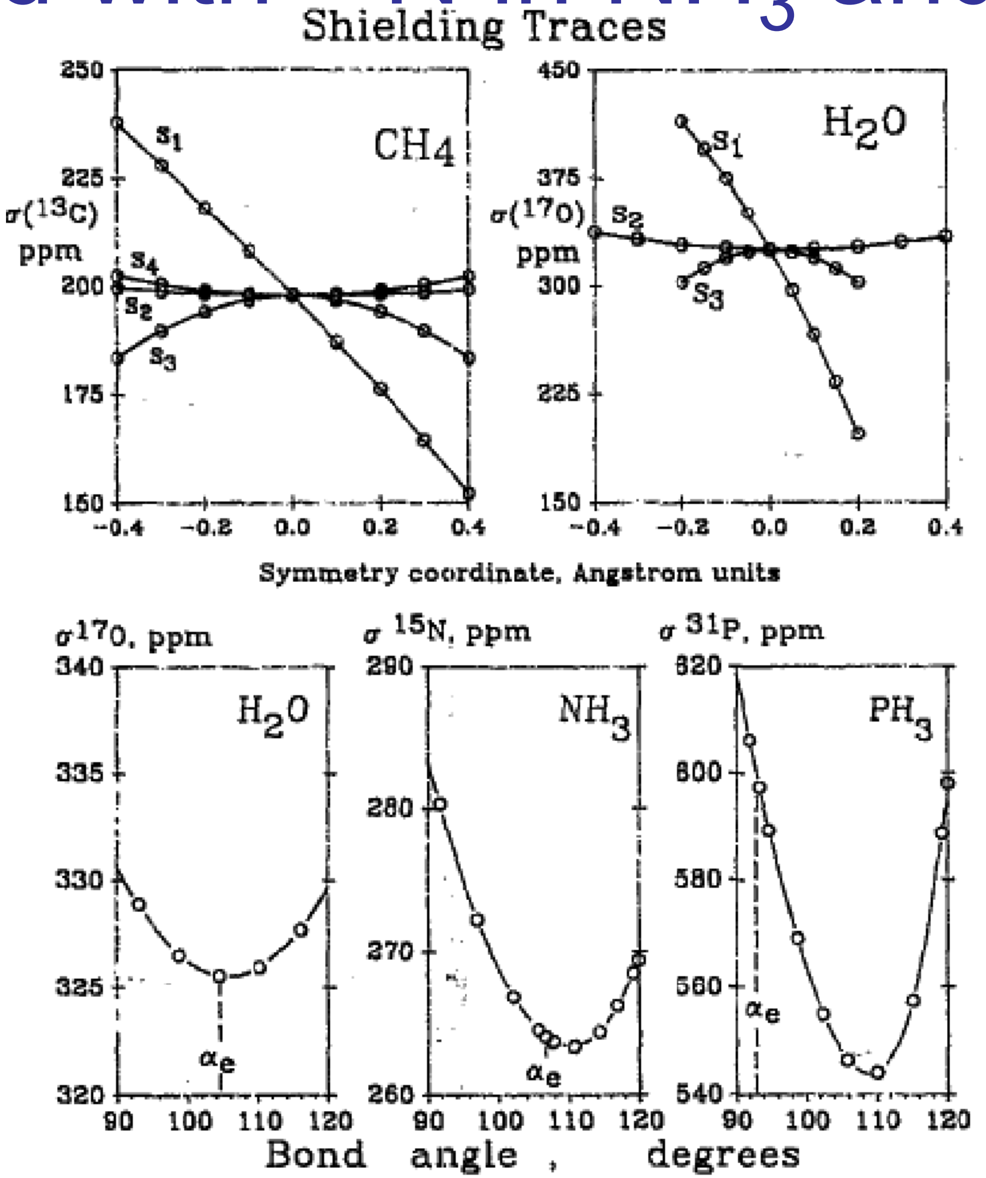
^{15}N shielding surface in NH_3 molecule



^{15}N and ^{31}P shielding function of the inversion coordinate in NH_3 and PH_3

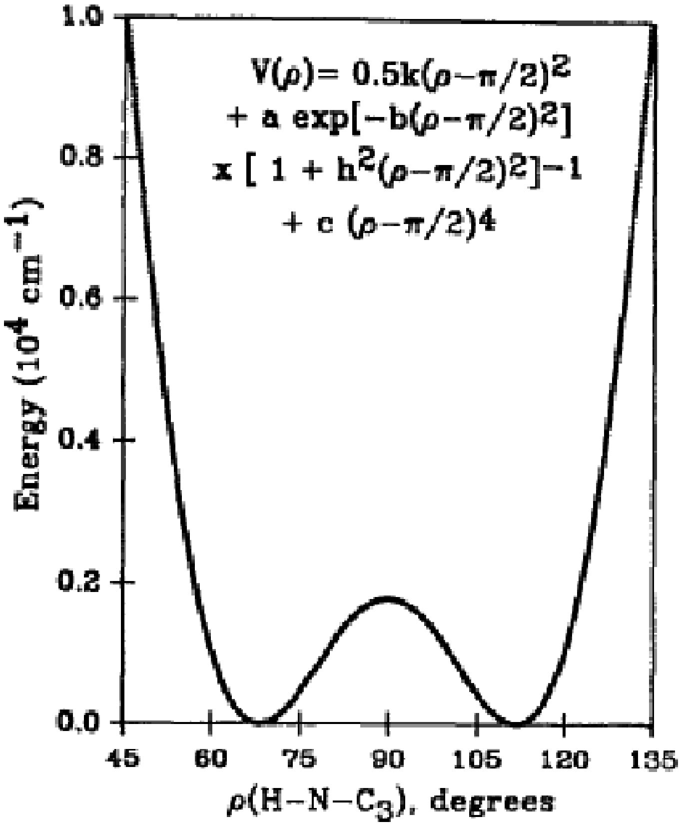


shielding surfaces for ^{13}C in CH_4, ^{17}O in H_2O compared with ^{15}N in NH_3 and ^{31}P in PH_3

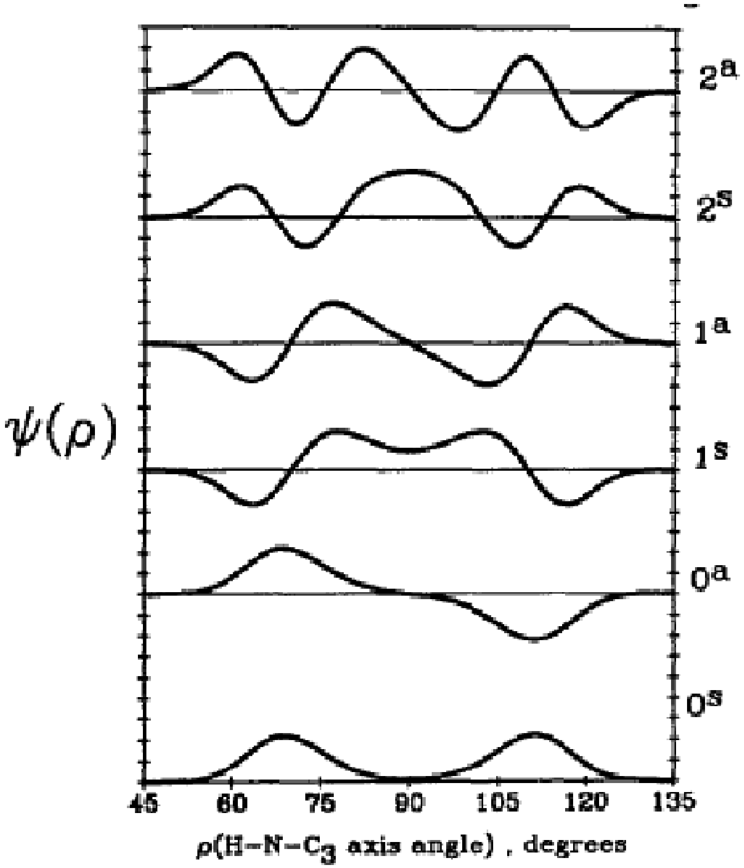


dynamic averages in polyatomic molecules

the inversion potential and its wavefunctions for NH_3

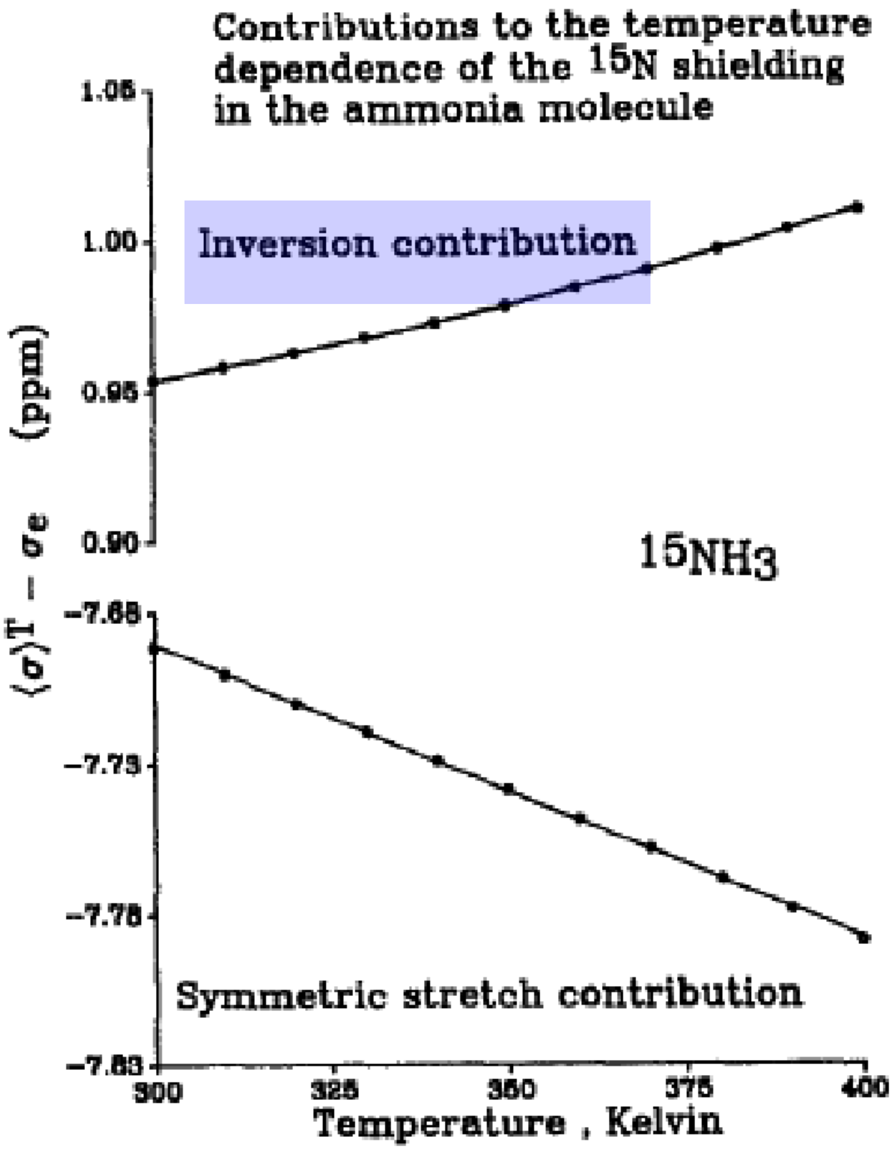


Inversion potential function of NH_3



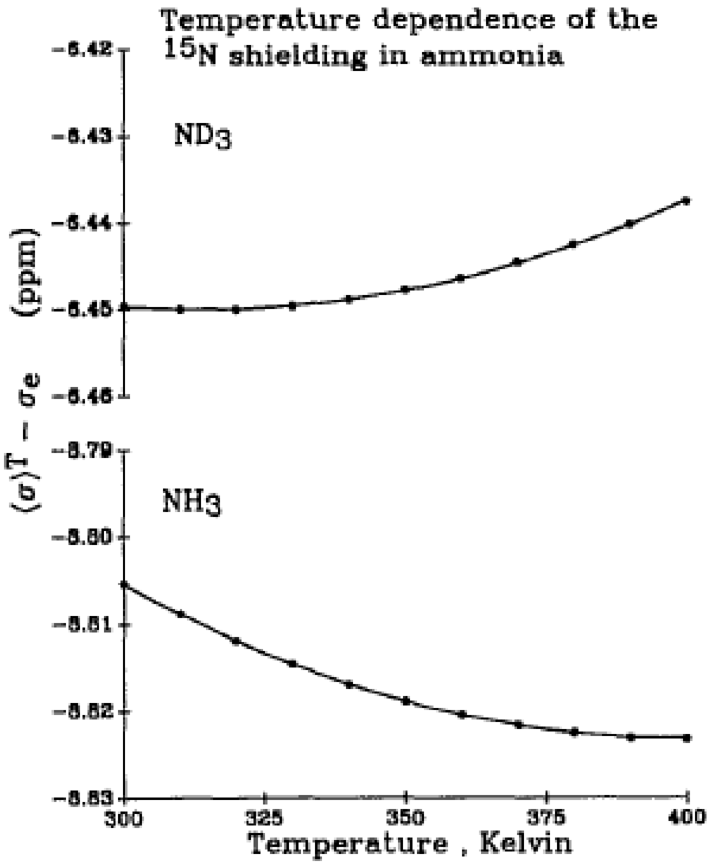
Inversion wavefunctions of NH_3

calculated T dependence of ^{15}N shielding in NH

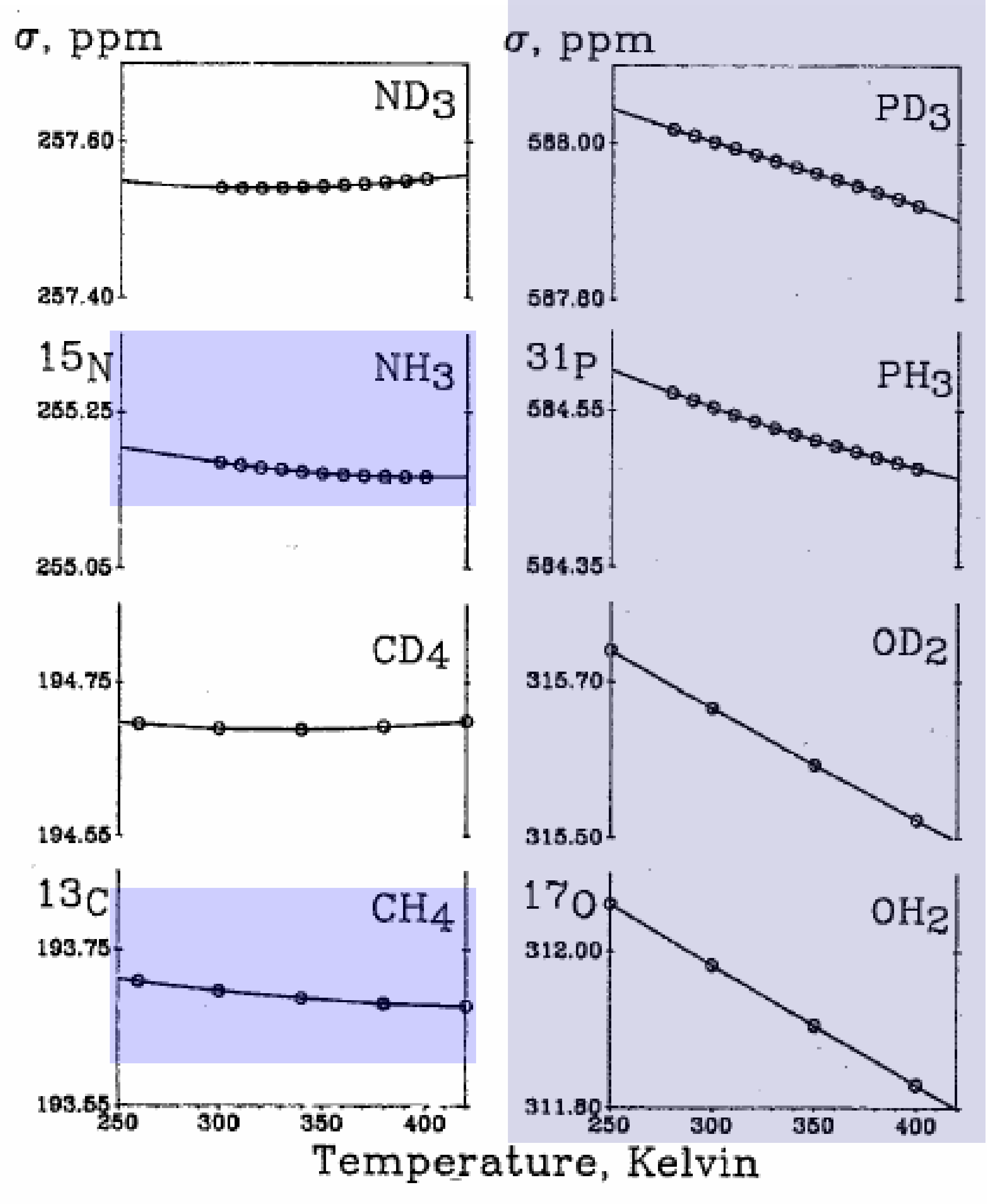


Contributions to the temperature dependence of the ^{15}N shielding in the ammonia molecule

calculated T dependence of ^{15}N shielding in NH_3 and ND_3



calculated temperature dependence for ^{15}N, ^{13}C, ^{31}P, ^{17}O



decreasing chemical shift with increasing T

for "central" atoms the T dependence is not simple to calculate

approximate analysis of ^{19}F temperature dependence

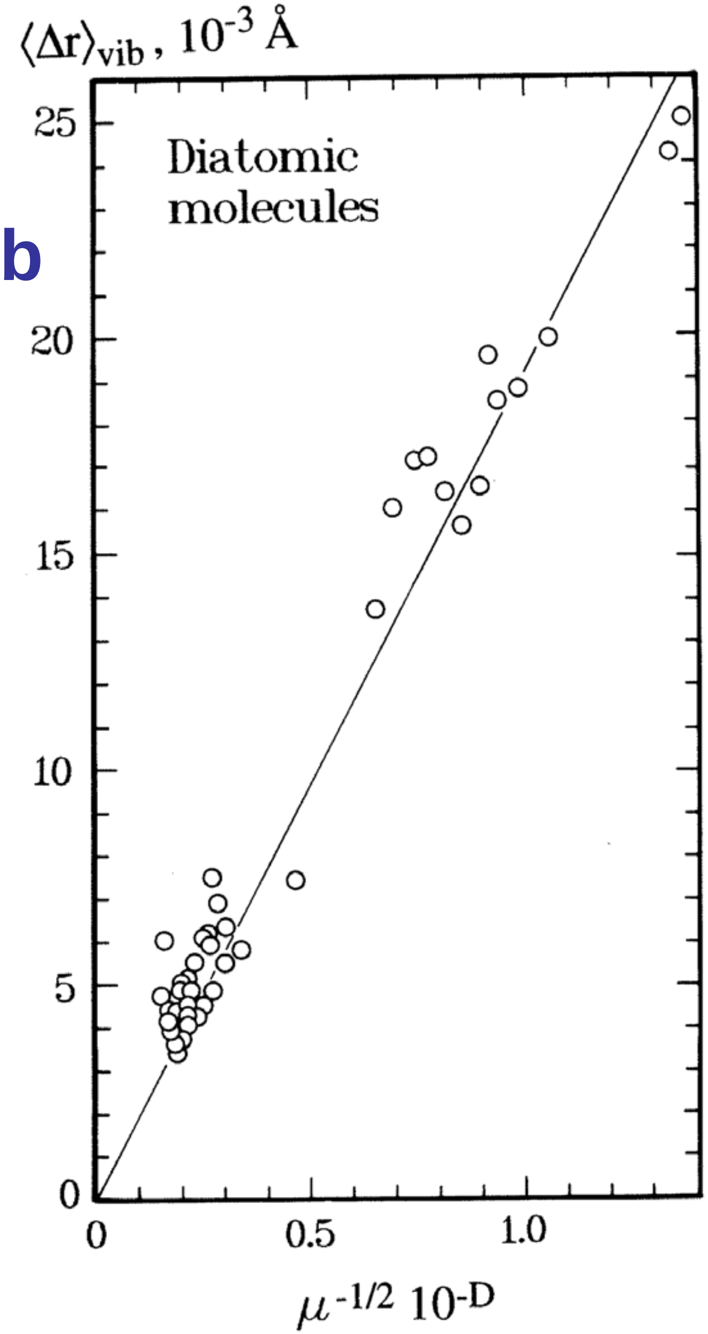
$$d\langle\sigma\rangle^{T} dT \simeq (\partial\sigma/\partial\Delta r)_e (d\langle\Delta r\rangle^{T}/dT)$$

$$+ (\partial\sigma/\partial\Delta\alpha)_e (d\langle\Delta\alpha\rangle^{T}/dT) + \ldots$$

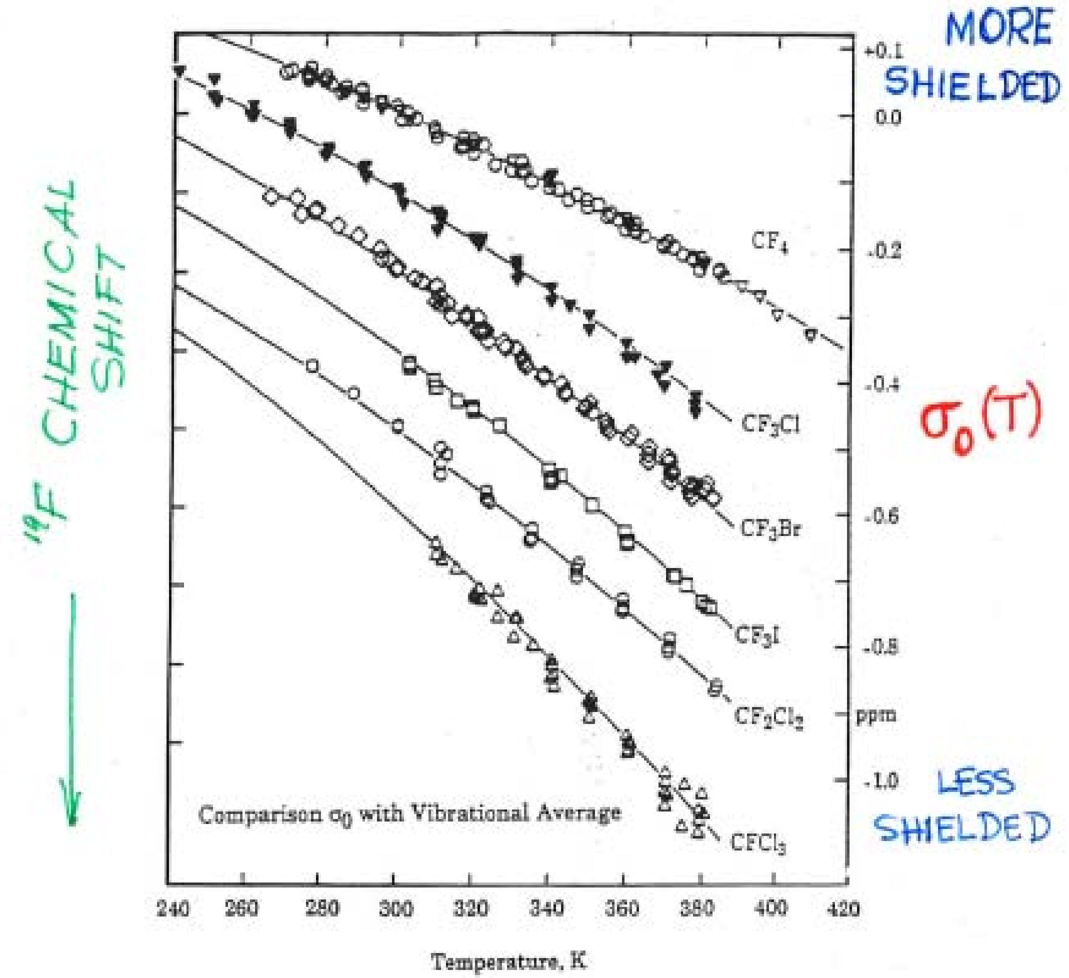
for nuclei of any terminal atom in a molecule, there is <u>one dominant bond stretch term</u> and the angle deformation terms are less important

can estimate $\langle\Delta r\rangle_{vib}$

from position of two atoms in the Periodic Table using Herschbach and Laurie parameters



calculated temperature dependence of ^{19}F using one parameter fit to isolated molecule data



$$d\langle\sigma\rangle^T dT \simeq (\partial\sigma/\partial\Delta r)_e (d\langle\Delta r\rangle^T/dT)$$

When system is not an isolated molecule, temperature dependence of intermolecular interactions come into play.

IV. intermolecular shifts in a constant volume homogeneous system

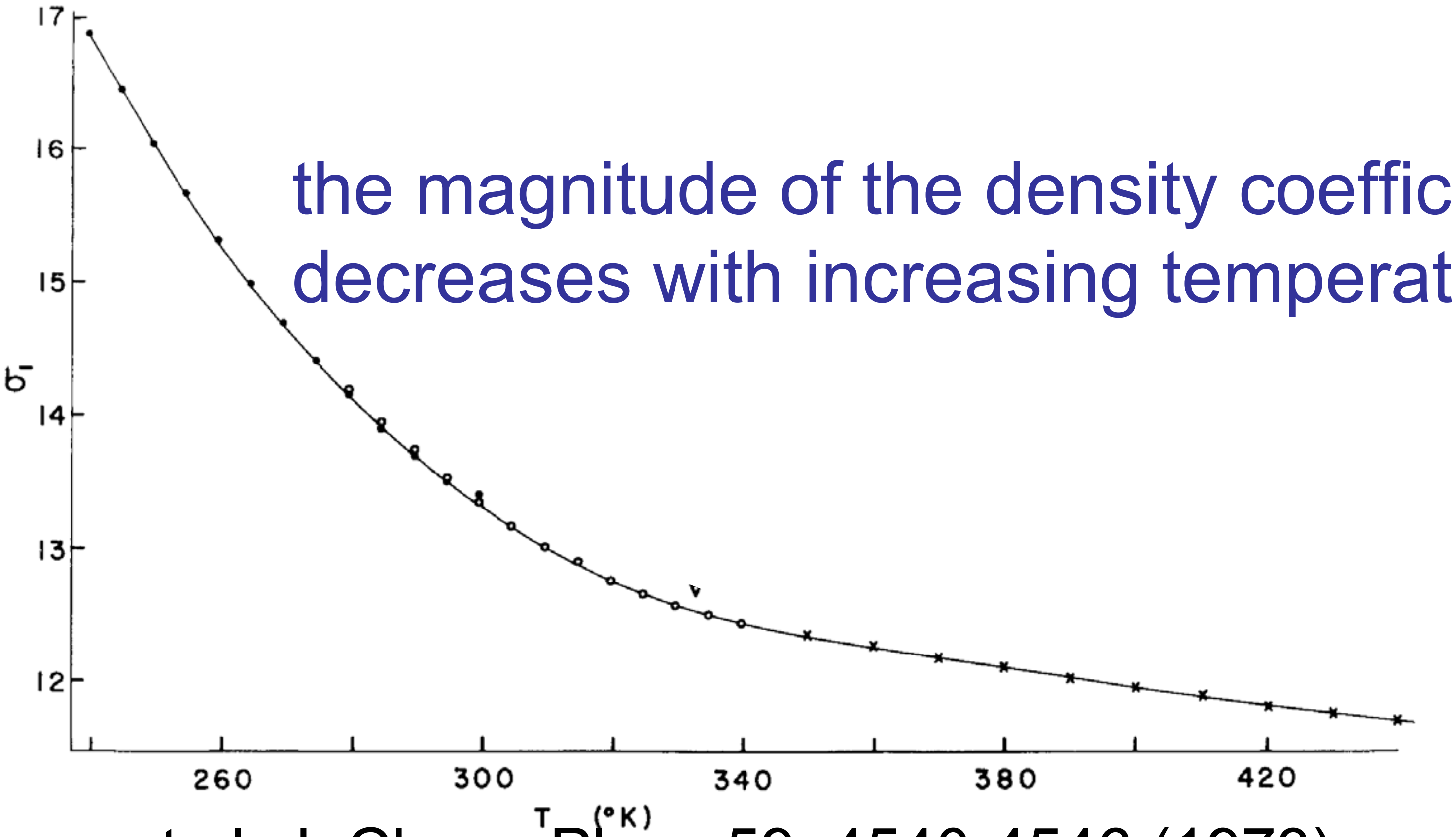
- In a sealed sample of fluid above the critical point or at *T,p* above the liquid-vapor equilibrium curve: the temperature dependence of the chemical shift comes entirely from that in the isolated molecule plus that due to the virial expansion of the shielding.

$$\sigma(T,\rho)=\sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \ldots$$

(see 'Intermolecular Chemical Shifts' for details)

(usually) increasing chemical shift with increasing density

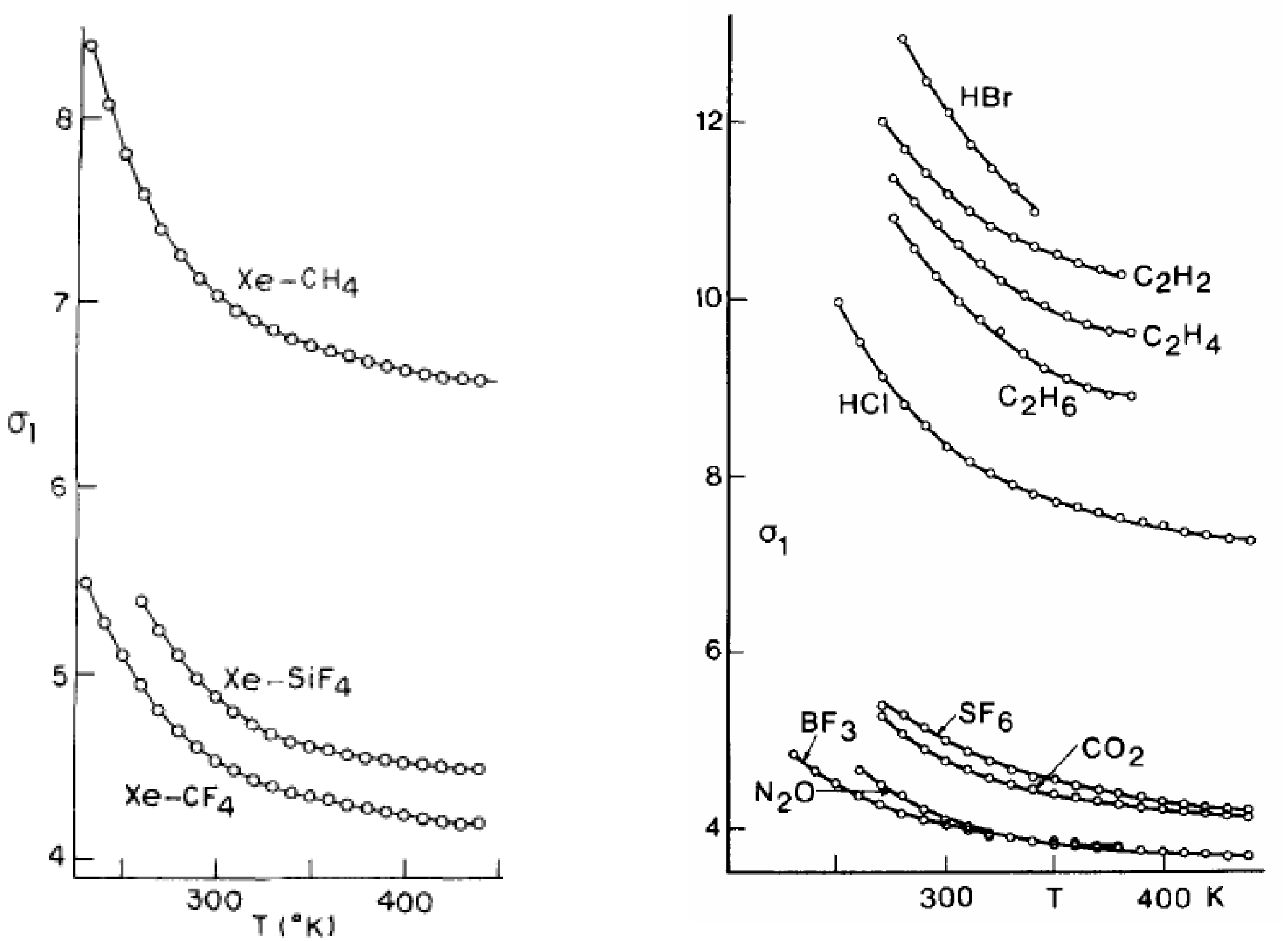
density coefficient of the ^{129}Xe chemical shift, the second virial coefficient of shielding, $\sigma_1(T)$



the magnitude of the density coefficient decreases with increasing temperature.

Jameson et al. J. Chem. Phys. 59, 4540-4546 (1973).

density coefficient of the ^{129}Xe chemical shift in various gases



Jameson et al. J. Chem. Phys. **65**, 3401-3406 (1976); J. Chem. Phys. **66**, 5226-5230 (1977).

V. intermolecular shifts in a constant pressure homogeneous system

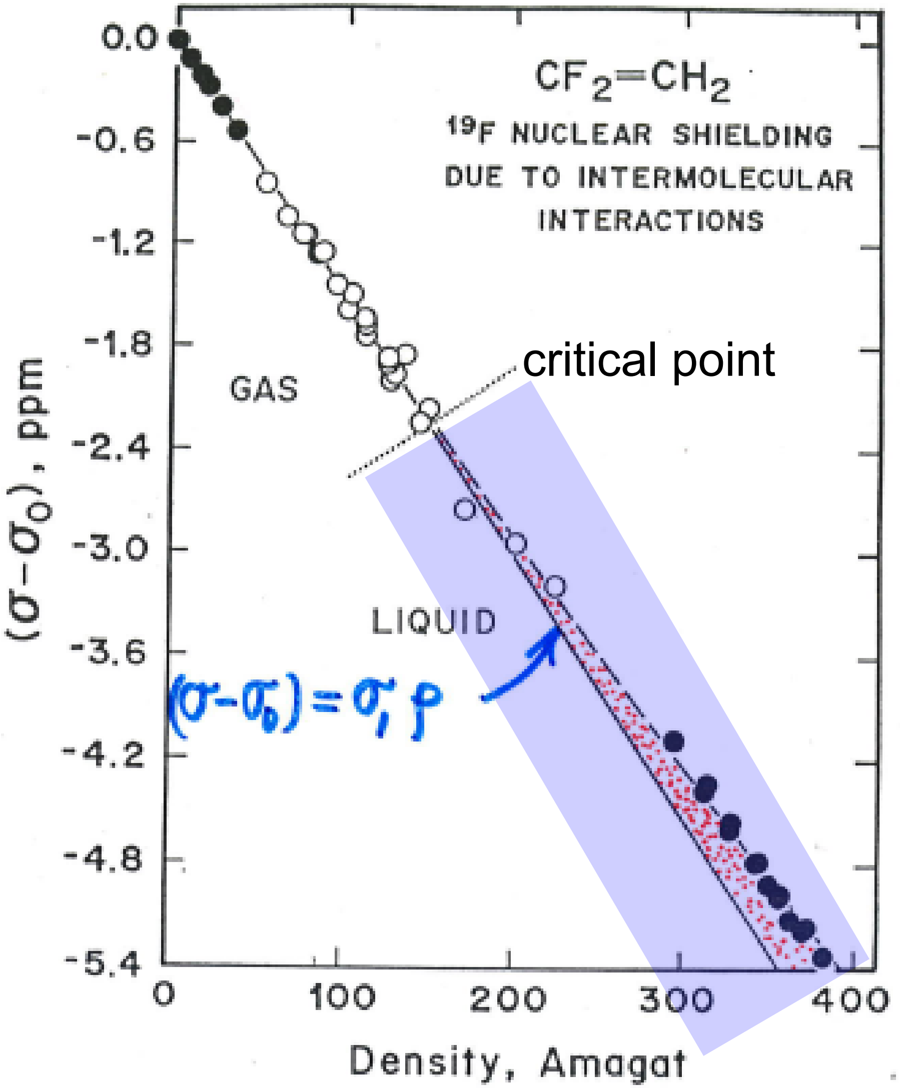
the major contribution from expansion of the liquid

$$\delta(T,\rho) \approx \delta_0(T) + \delta_{1\mathrm{eff}}(T)\,\rho_{\mathrm{LIQ}}(T) + \ldots$$

where ρ_{LIQ} is the number density of molecules in the liquid and $\delta_{1\mathrm{eff}}(T)$ is the density coefficient of the chemical shift in cases where a linear dependence on density is observed.

$^{19}\mathrm{F}\ \ \sigma(T,\rho)-\sigma_0(T) \approx \sigma_{1\mathrm{eff}}(T)\ \rho_{\mathrm{LIQ}}(T) + \ldots$

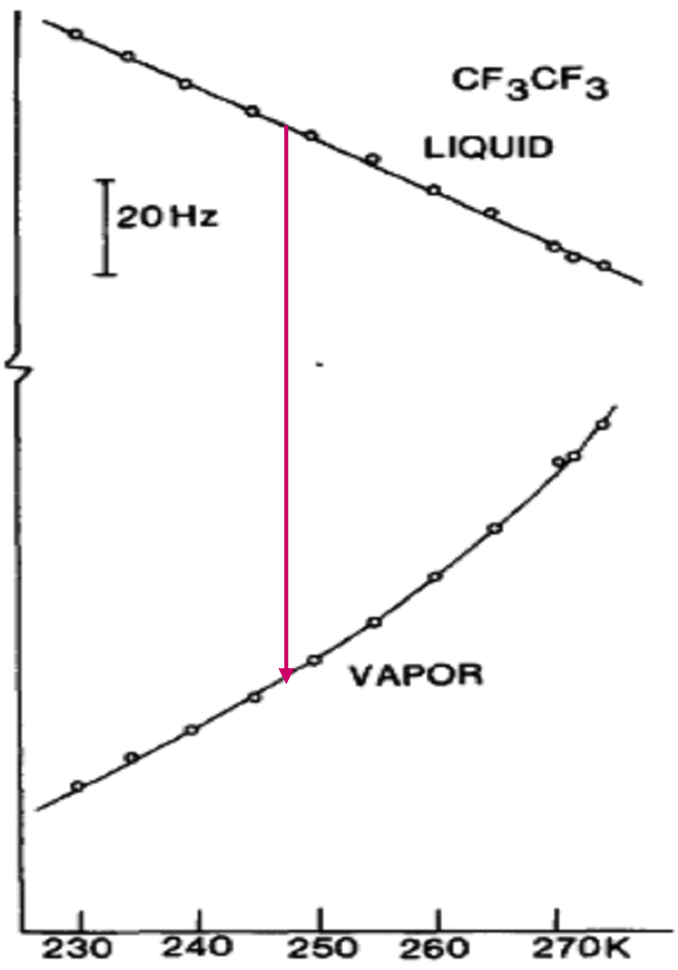
increasing chemical shift with increasing density

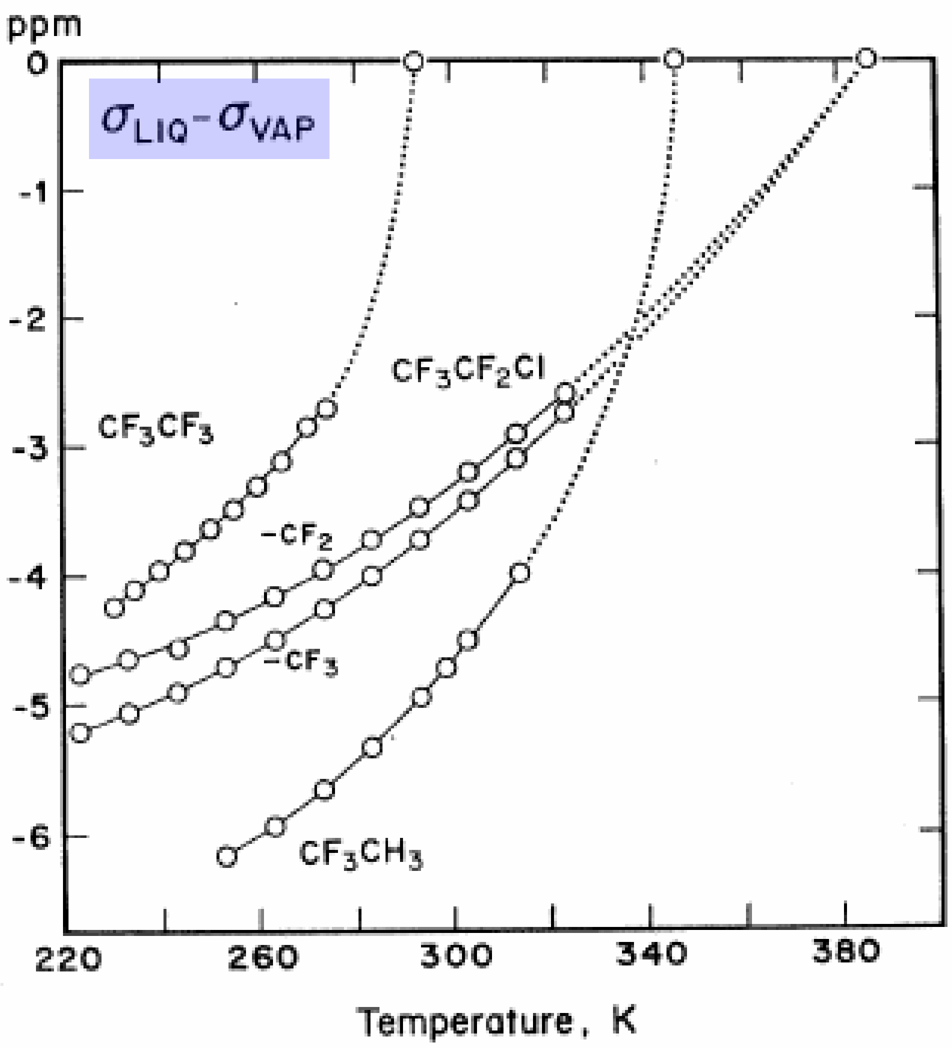


nearly linear dependence on density of liquid, but smaller slope

from gas to liquid shifts: $\sigma(T,\rho)-\sigma_0(T) \approx \sigma_{1eff}(T)\,\rho_{LIQ}(T) + \dots$

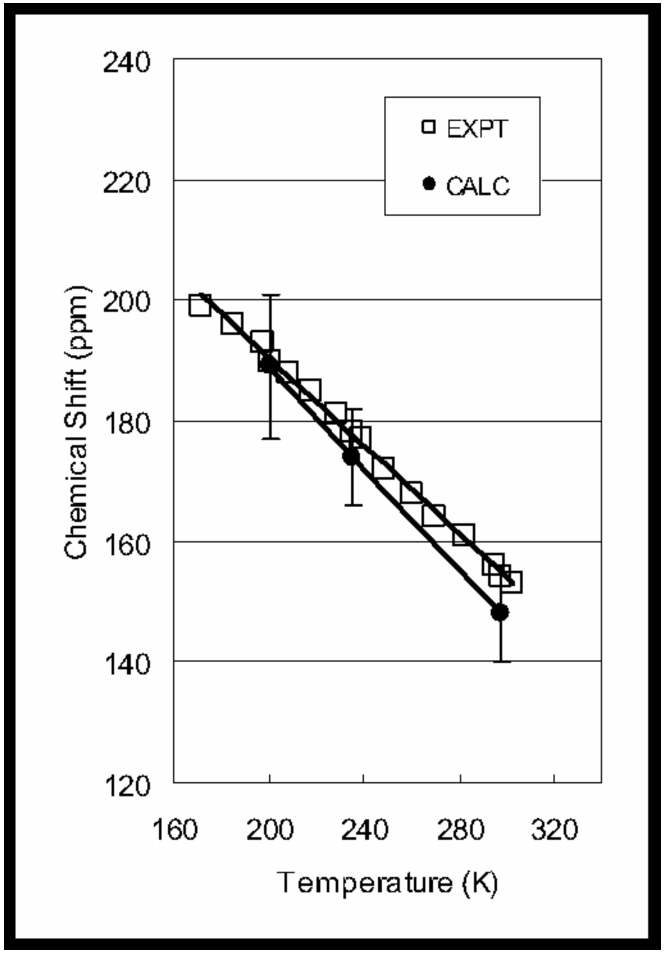
increasing chemical shift ⟶



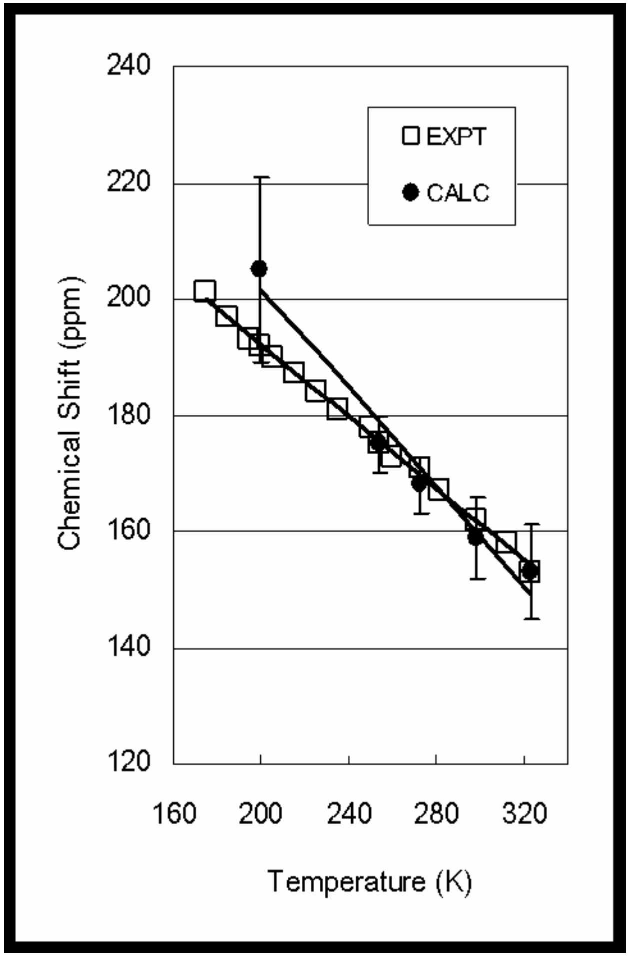


Xe chemical shift temperature dependence in solution

n-pentane :



n-hexane :

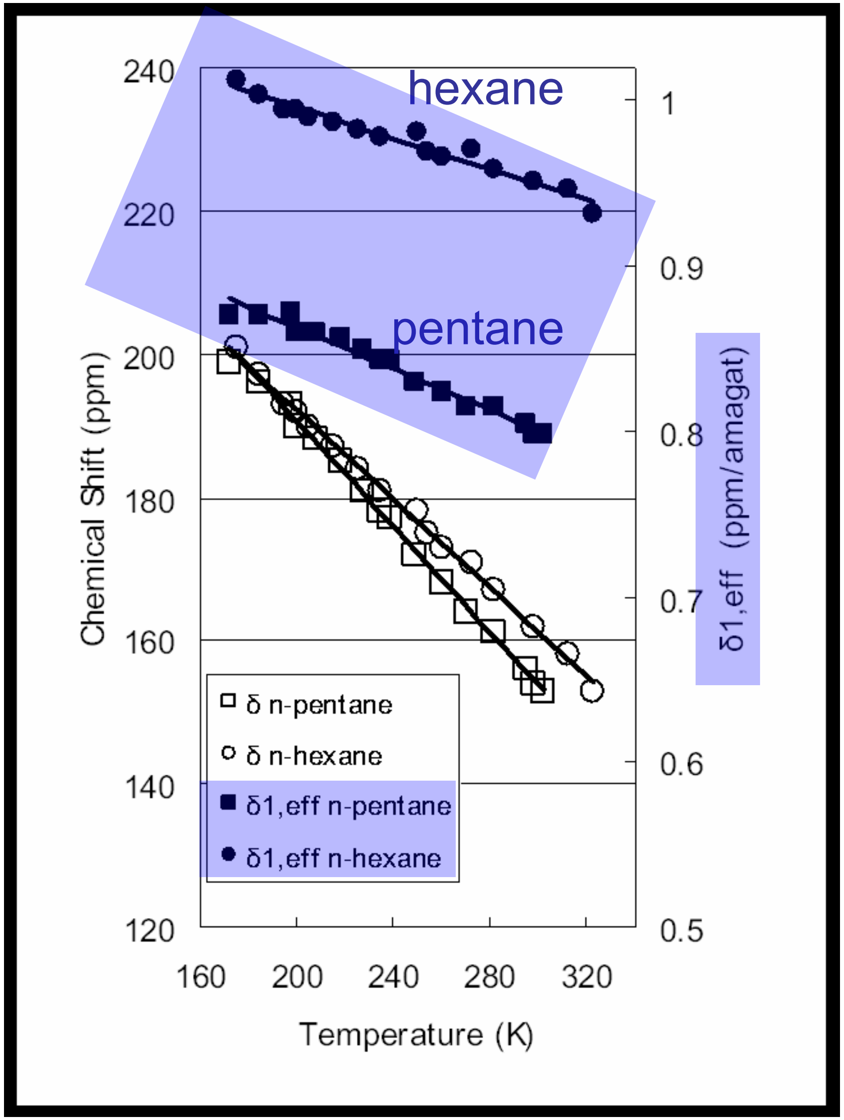


Molecular Dynamics simulations results

J. Phys. Chem. C, 111, 15771-15783 (2007).

Contributions to the temperature dependence of Xe chemical shifts in solution

T dependence of the solvent density is responsible for most of the observed steep T dependence of Xe chemical shifts in solution. The remainder is from T dependent Xe Interactions with alkane, $\delta_1(T)$



divide out the density to get δ_{1eff} just as in pure liquids

VI. intermolecular shifts in heterogeneous systems: one in a cage, *n* in a cage

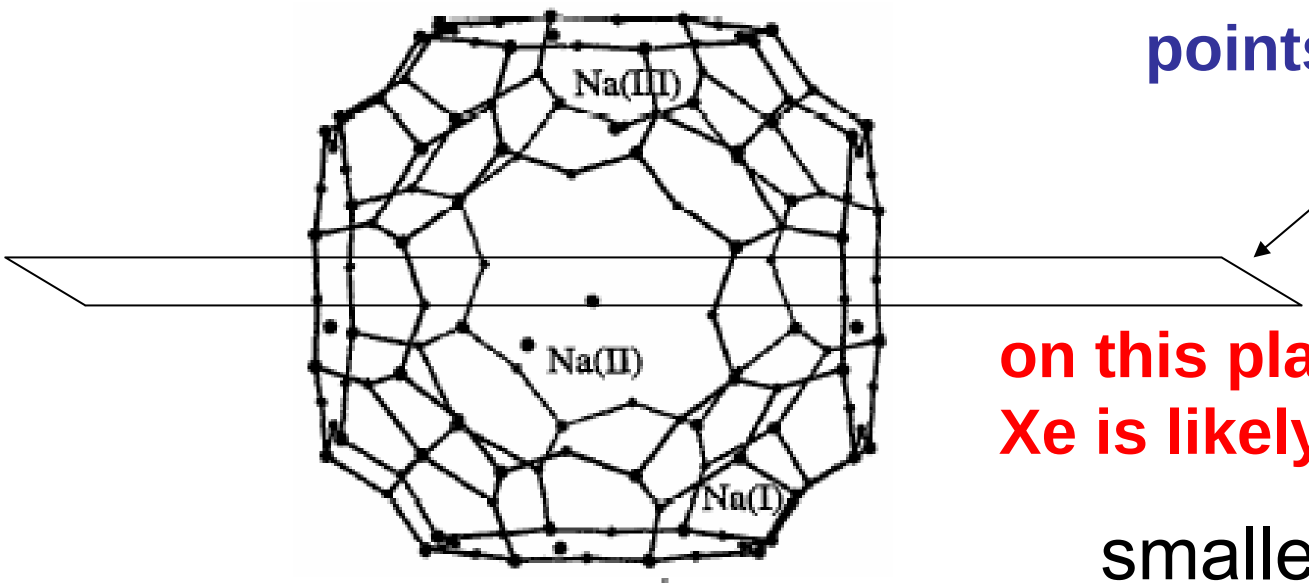
- one Xe in a cage: governed by probability distribution functions changing with temperature
- compare with one Xe in a flexible cage governed by (a) probability distribution functions changing with temperature, and (b) dynamics of cage atoms changing with temperature
- n Xe in a cage governed by (a) one-body probability distribution functions changing with temperature, and (b) two-body distribution functions changing with temperature

first consider one Xe in a cage, no Xe-Xe interactions

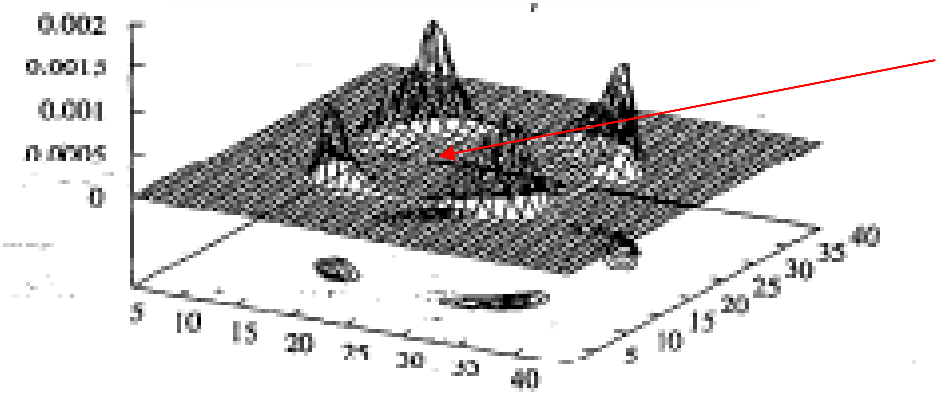
- What is the expected temperature dependence of the chemical shift?
- This depends on the size of the cage relative to the diameter of the Xe atom
- in a small cage, the potential energy surface for the Xe is lowest in the center
- in a larger cage, there are potential energy minima for the Xe at points ~ 4 Å to the wall, less favorable at the center

Xe in a rigid cage Na*A*

Let us take a look at points on this plane



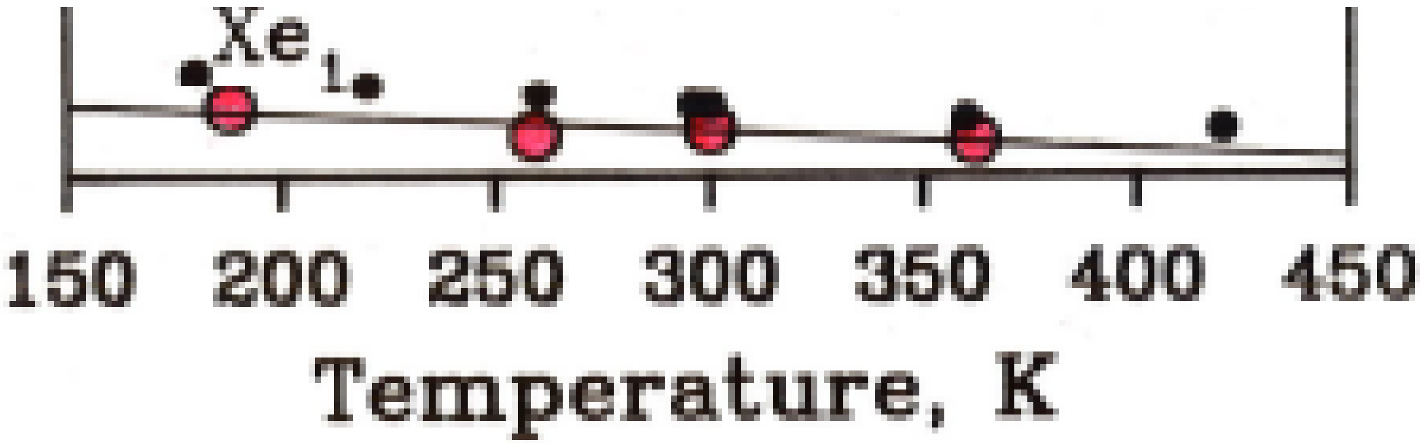
on this plane, where is Xe is likely to be found?



smaller probability near center of cage where chemical shift is lower

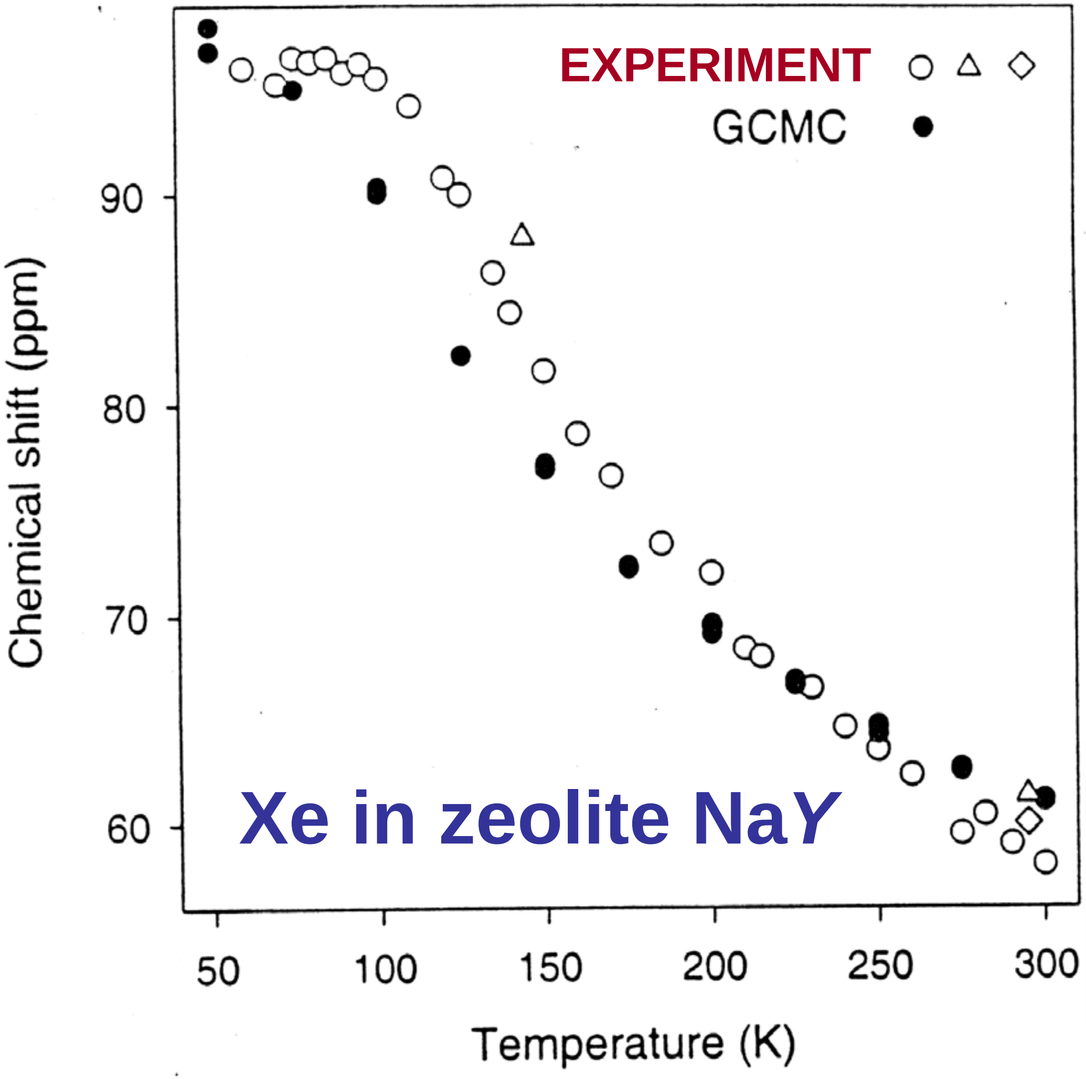
With increase in temperature, probability density spreads out, including more of central region where chemical shift is lower

at higher T, Xe can explore regions of higher potential energy and smaller chemical shift



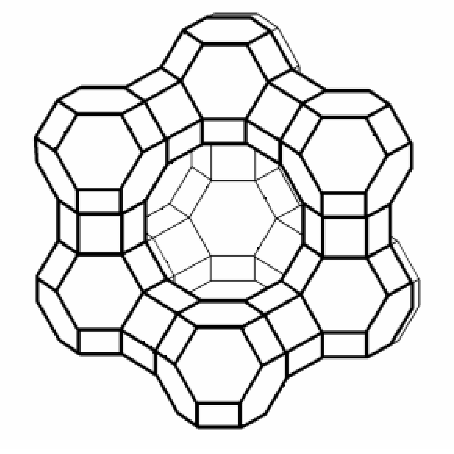
Xe-cage contribution only. This intermolecular chemical shift decreases with increasing temperature

Temperature dependence of ^{129}Xe chemical shift at near-zero loading

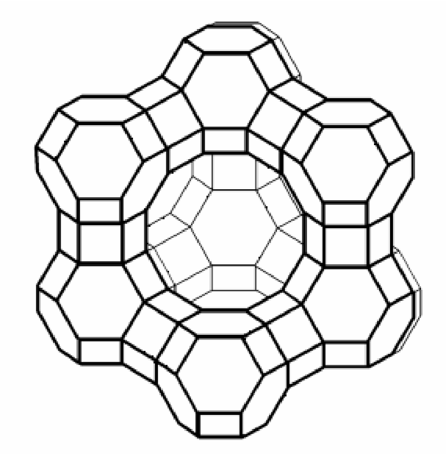


Xe in zeolite Na*Y*

GCMC simulations
Jameson and Kostikin, 2001



○ Expt., Pietraβ et al. 1999 $\langle n \rangle_{Xe} = 0.25$ atoms/cage
△ Expt., Cheung, 1988 $\langle n \rangle_{Xe} = 0.2$ atoms/cage
◇ Expt., S. B. Liu, 1994 $\langle n \rangle_{Xe} = 0.2$ atoms/cage
● GCMC calculations $\langle n \rangle_{Xe} = 0.250(5)$ atoms/cage

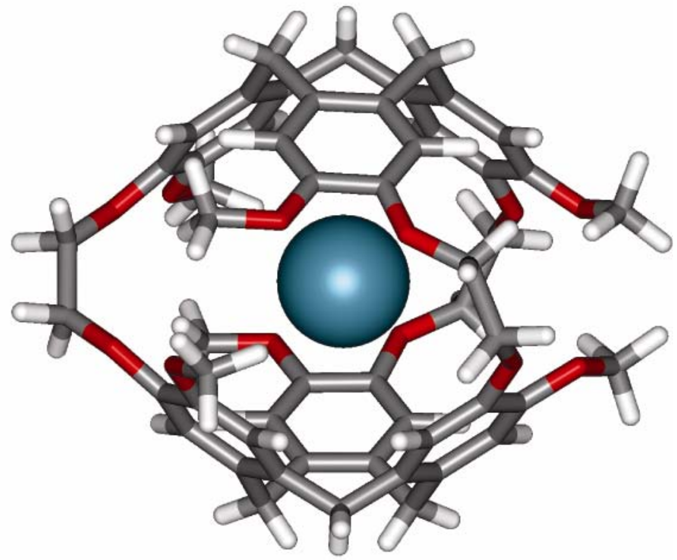


Xe at near zero loading in Na*Y*

At low temperatures, Xe spends most of its time in the low potential energy regions next to the walls of the large cages, which correspond to higher chemical shifts. As temperature increases, the Xe probability density spreads out over more regions farther away from the walls, which correspond to lower chemical shifts.

This is the same trend as for one Xe in Na*A* cage

Xe in a small flexible cage

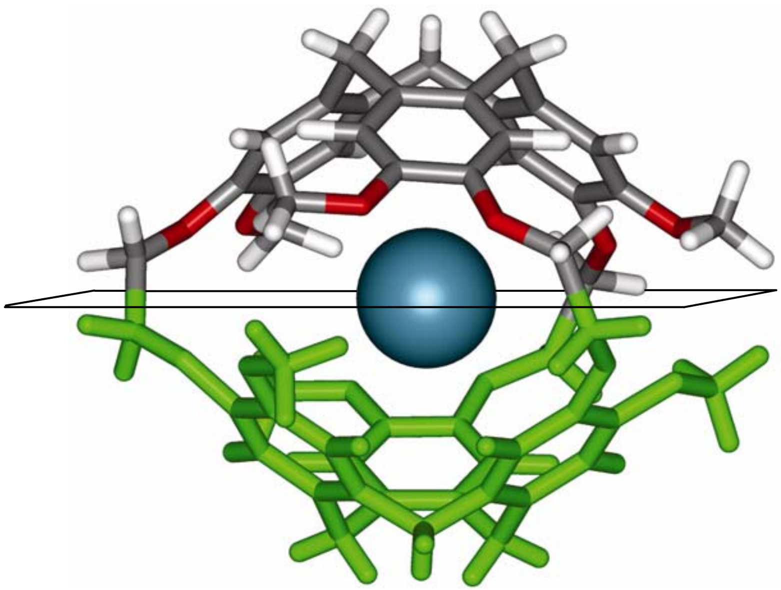


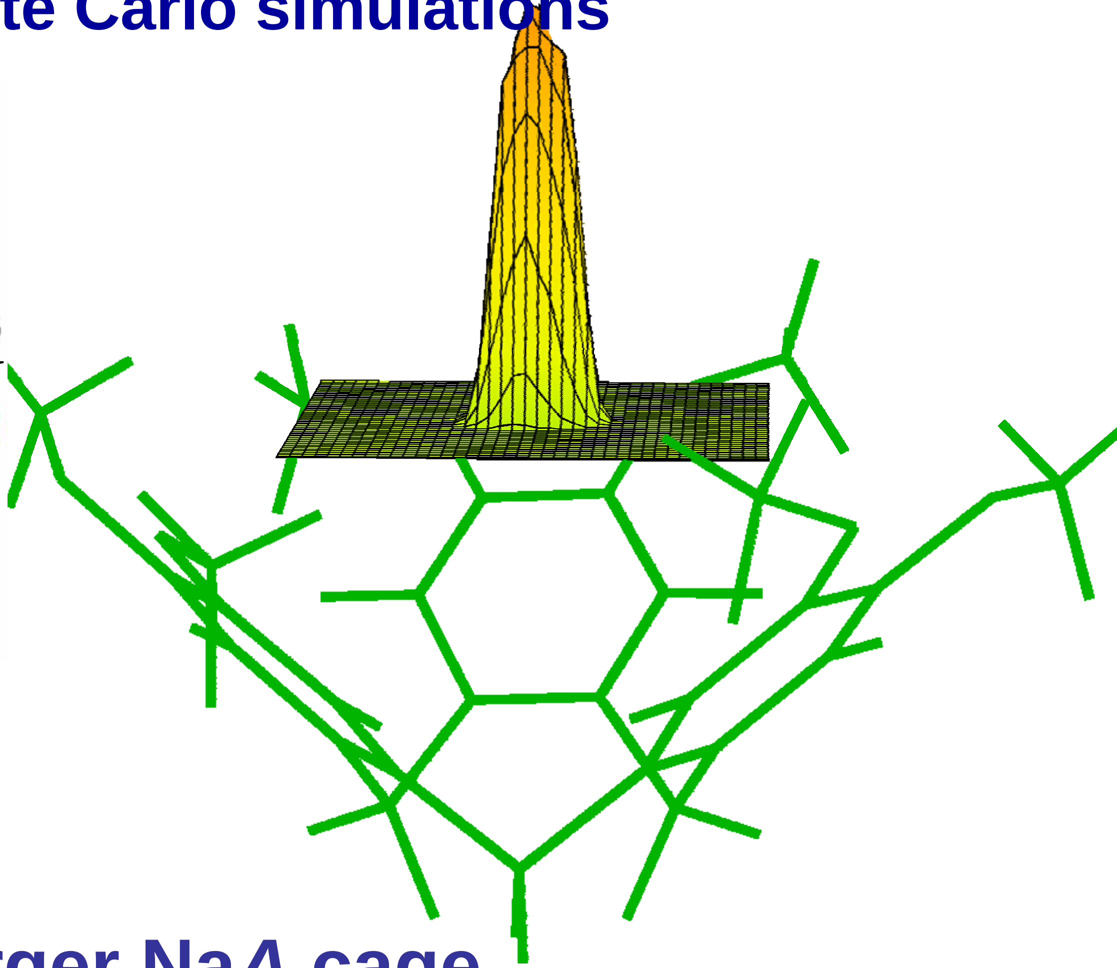
two contributions:

- Xe probability distribution within the cage changes with T
- cage deformation (away from nearly spherical) is more pronounced at higher T, leads to closer Xe interactions with wall atoms

One-body distribution function for Xe@cryptoA

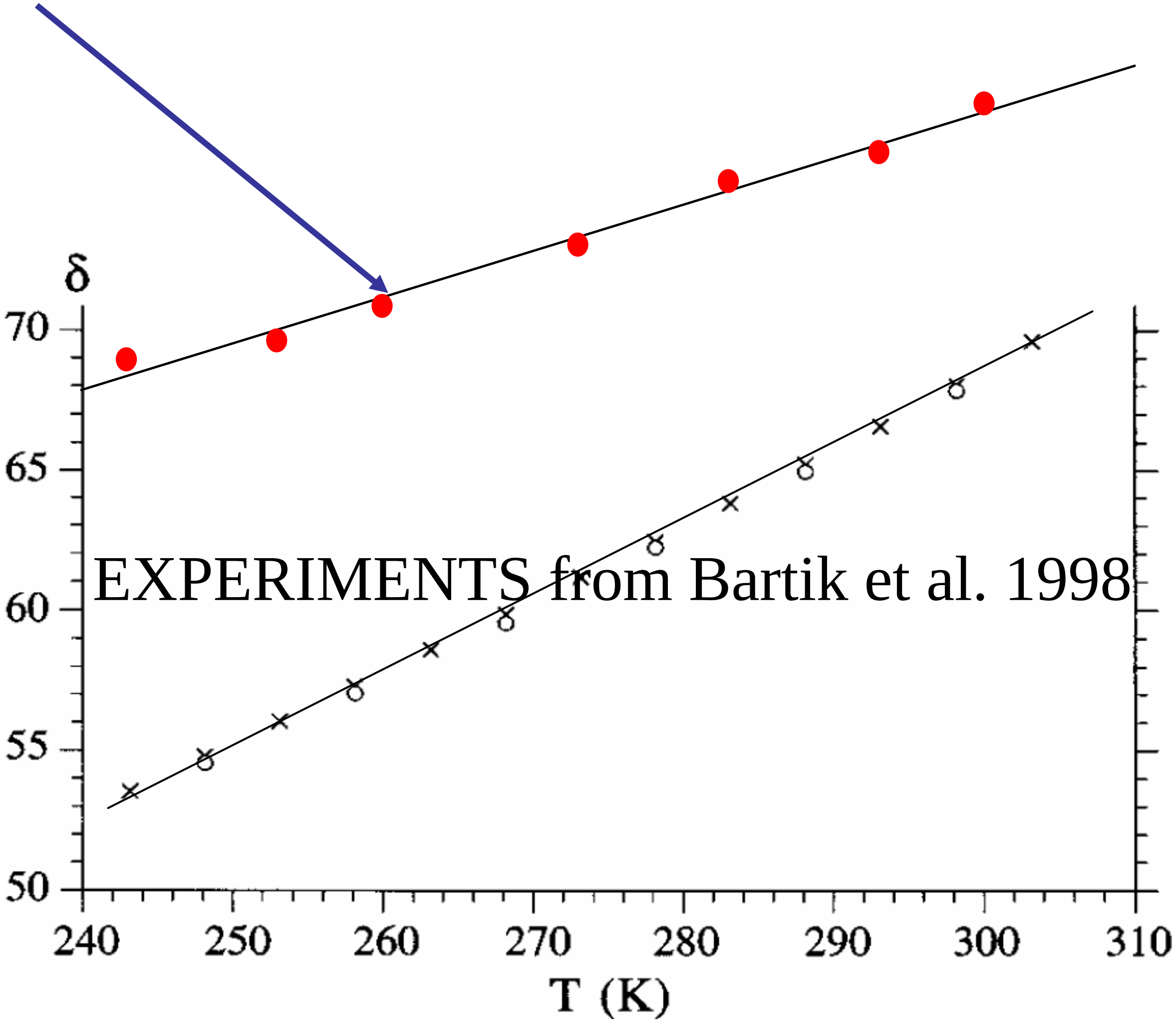
from Monte Carlo simulations





**Unlike Xe in the larger Na*A* cage,
for Xe in this smaller cage, the probability
is highest in the center, and lower near the walls.**

Temperature dependence of Xe@cryptoA not including cage deformation



EXPERIMENTS from Bartik et al. 1998

- ● **Monte Carlo SIMULATIONS**
  D. N. Sears and C. J. Jameson, 2003

Our Monte Carlo SIMULATIONS

T, K	δ , ppm
300	78.77
293	76.35
283	75.31
273	73.04
260	70.73
253	69.62
243	68.94

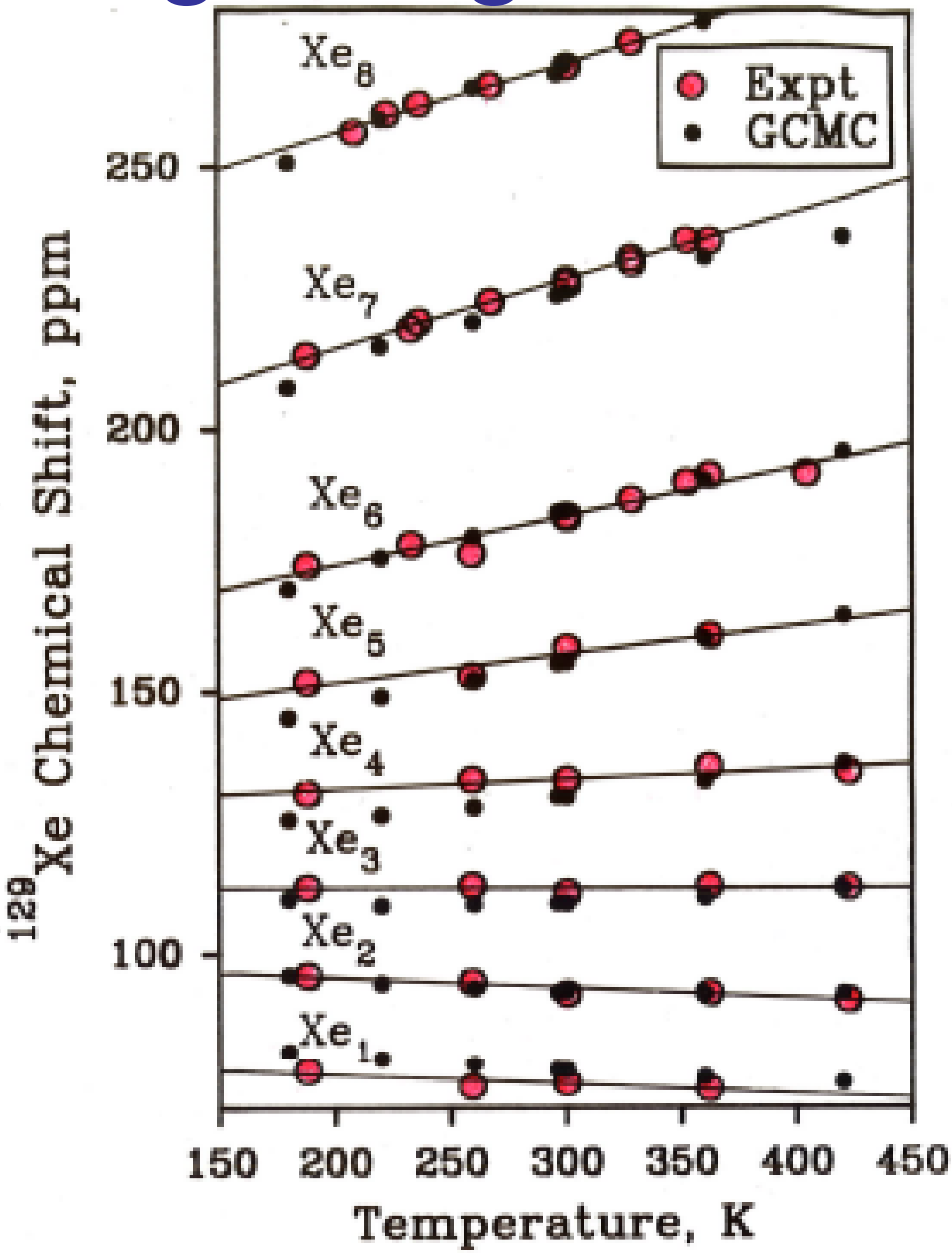
Xe-Xe chemical shift contributions

- with increasing number of Xe atoms in the same cage, Xe-Xe contributions increase, leading to higher chemical shifts
- for a fixed number of Xe atoms in the cage, temperature dependence is a combination of Xe-Xe contributions changing with T and Xe- wall contributions changing with T

n Xe atoms in a rigid cage

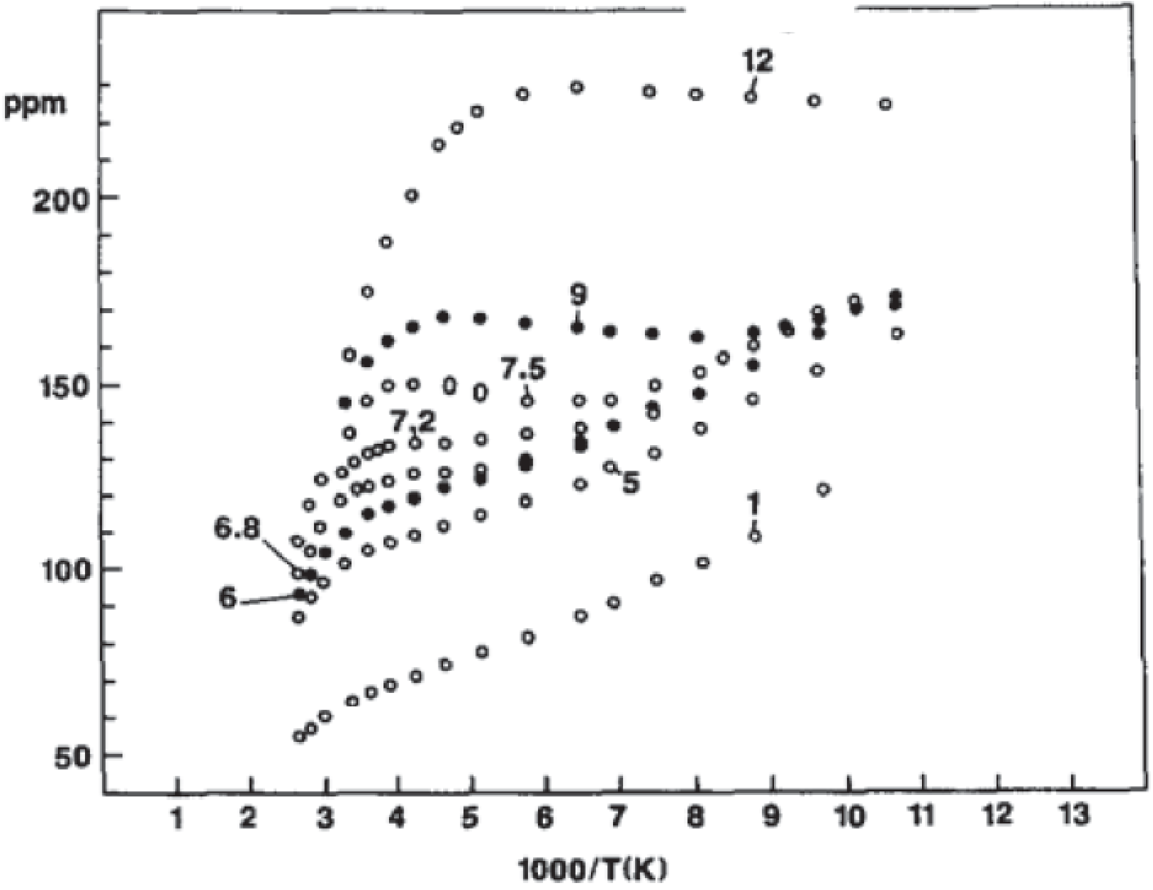
Xe-Xe contributions dominate over Xe-cage contributions at *n* large enough.

Xe-Xe interactions explore regions higher up on repulsive Xe-Xe potential wall at higher T, these correspond to larger chemical shifts.



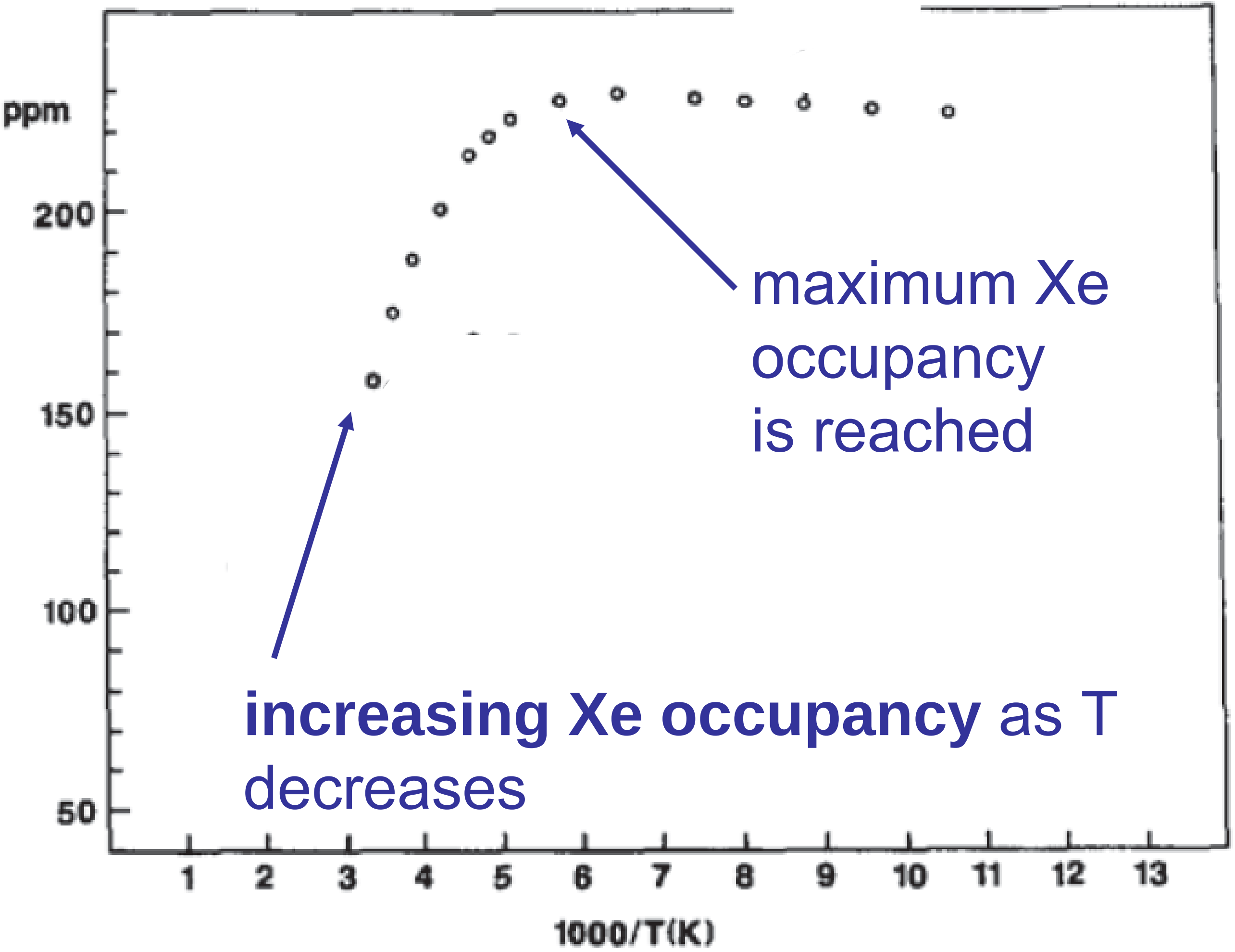
VII. heterogeneous systems: changing occupancy in a channel

dominated by changes in adsorption isotherm with increasing temperature, that is, **Xe occupancy changes markedly with temperature**



J.A. Ripmeester,
C. I. Ratcliffe
Anal. chim. Acta
283, 1103 (1993)

For a sealed sample of Xe in NaY, steep increase in Xe chemical shift from **increasing Xe-Xe contributions**

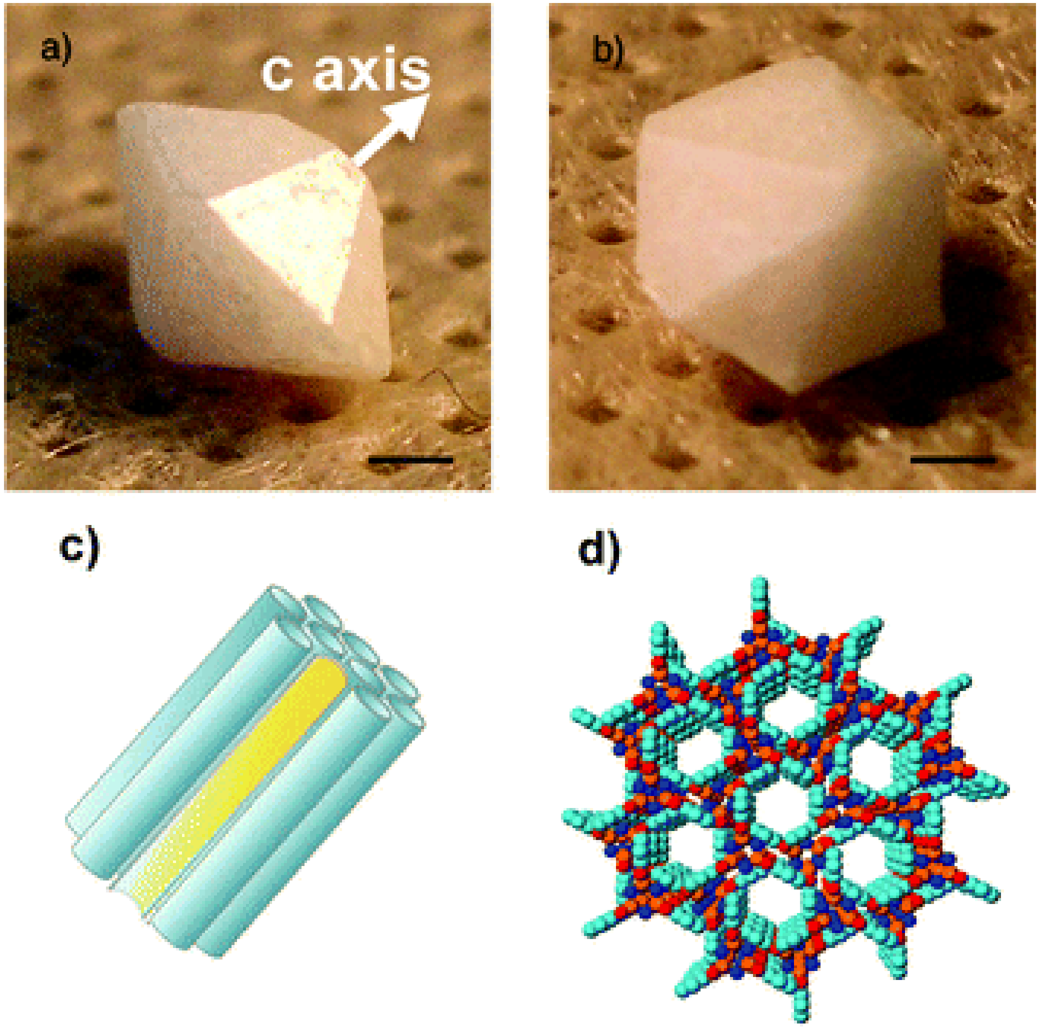


maximum Xe occupancy is reached

increasing Xe occupancy as T decreases

single crystal experiments

A. Comotti, S. Bracco,L. Ferretti, M. Mauri, R. Simonutti and P. Sozzani Chem Commun 2007, 350-352



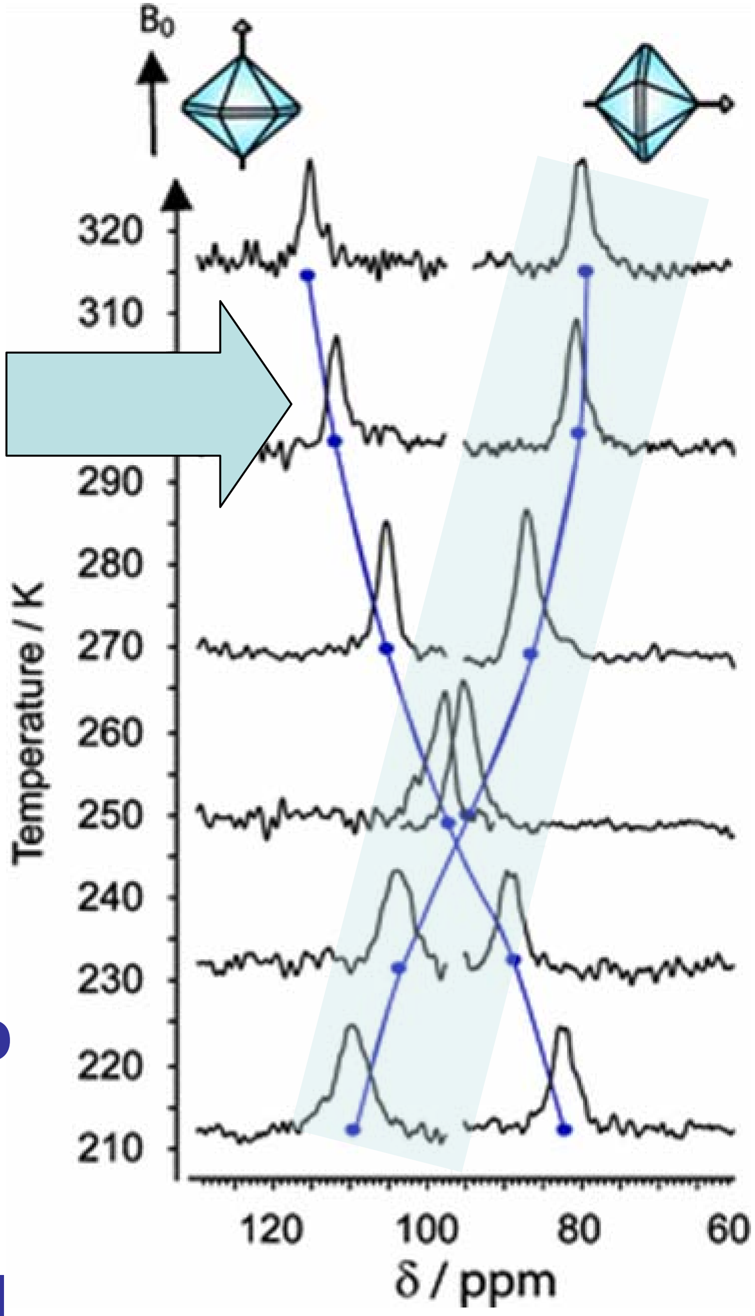
continuous flow

HP ^{129}Xe NMR

θ

δ || not dependent on Xe loading

increases with increasing T. This has to do with the constrictions in the channel



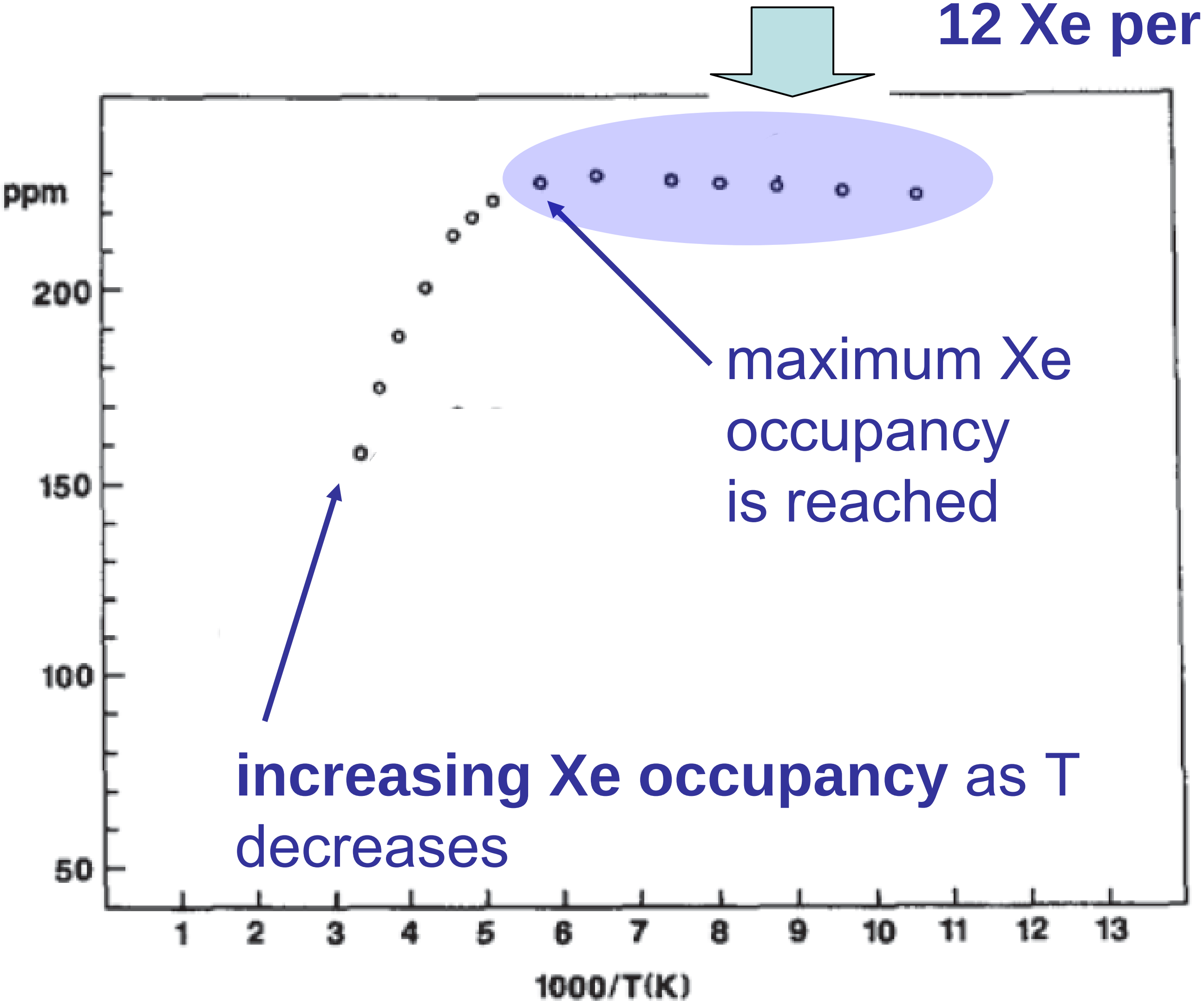
δ⊥ increases Xe-Xe contributions increase with increasing Xe occupancy as T decreases

A. Comotti, S. Bracco, L. Ferretti, M. Mauri, R. Simonutti and P. Sozzani Chem. Commun. 2007, 350-352

observe temperature dependence at fixed Xe occupancy

- Xe in NaY at full occupancy
- Xe in silicalite at full occupancy

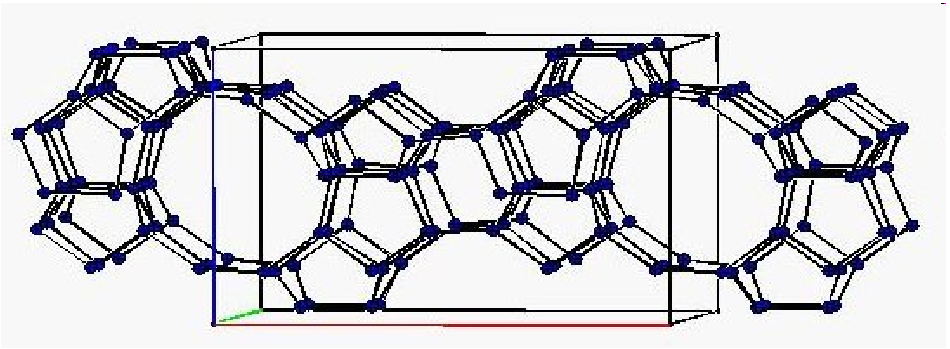
Xe in NaY at full occupancy



12 Xe per unit cell

maximum Xe occupancy is reached

increasing Xe occupancy as T decreases



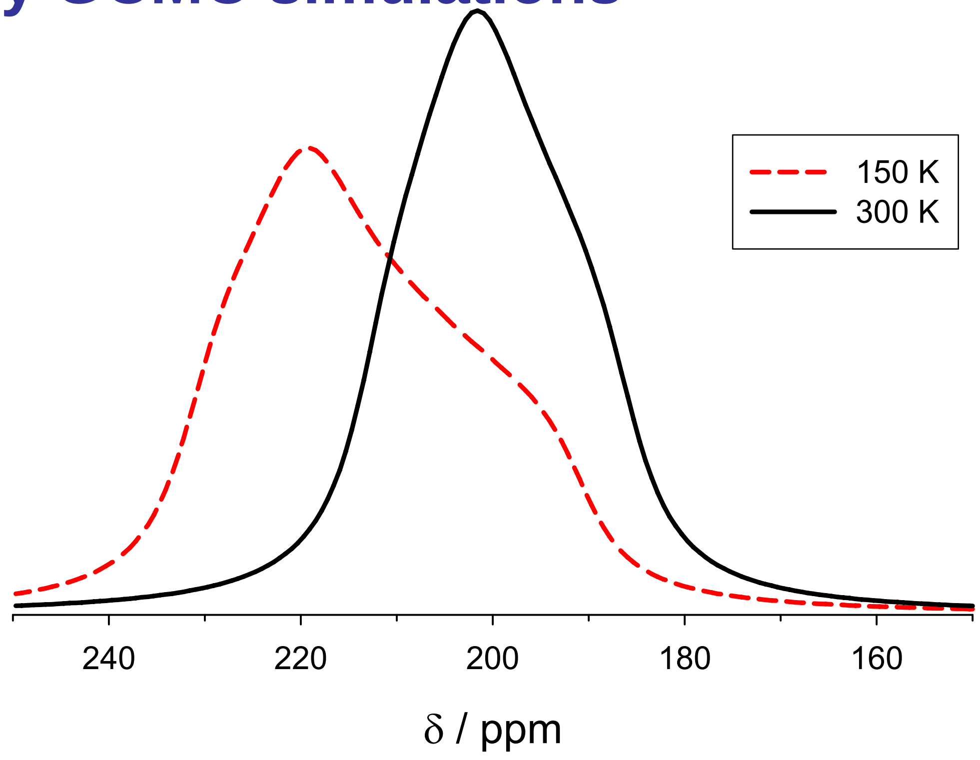
Xe at full loading
(16 Xe per unit cell)
in silicalite

The anisotropic environment of silicalite gives rise to 3 unique tensor components primarily arising from Xe-Xe contributions. Two of the components change dramatically with temperature, while the smallest component hardly changes. The changes in the Xe-Xe pair distribution function with temperature predicted by the Monte Carlo calculations reproduce the observed changes in line shape.

Xe line shapes at full occupancy

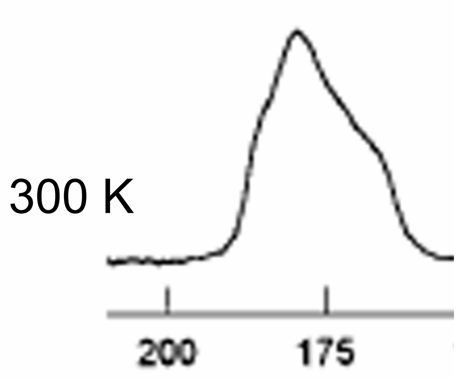
are well reproduced by GCMC simulations

Temperature dependence with no change in $\langle N \rangle_{Xe}$

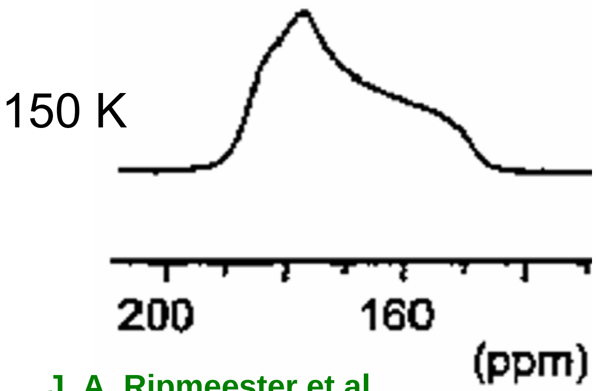


CALCULATIONS

Jameson 2003



Jameson et al.
J. Phys. Chem. B **1997,** *101,* 8418



J. A. Ripmeester et al.
J. Am. Chem. Soc. **2001**, 123, 10399

EXPERIMENTS

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